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THE

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Theoretical Physics

CONDUCTED WITH THE CO-OPERATION
OF THE
AMERICAN PHYSICAL SOCIETY
BY
EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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CONTENTS TO VOLUME XXXIII.

CLXXXII. JULY, 1911.

The Nature of Light Action in Selenium. F. C. BROWN 1
On the Dissolution of a Metal in a Binary Solution, one Component Acid. ARDEN RICHARD JOHNSON 27
The Positive Potential of Aluminum as a Function of the Wave-length of the Incident Light. J. R. WRIGHT 43
A Method of Measuring the Fluctuations in a Rapidly Varying Resistance. F. C. BROWN and W. H. CLARK 53
Increase of Magnetic Induction in Nickel Bars due to Transverse Joints. E. H. WILLIAMS 60
On the Fusion of Carbon. O. P. WATTS and C. E. MENDENHALL 65
On the Presence in Point Discharge of Ions of Opposite Sign. JOHN ZELENY 70
Notes on Optical Pyrometry. C. E. MENDENHALL 74
Temperature Coefficients of Electrical Resistance. III. A. A. SOMERVILLE 77

CLXXXIII. AUGUST, 1911.

A Verification of the Theory of Brownian Movements and a Direct Determination of the Value of *NE* for Gaseous Ionization. HARVEY FLETCHER 81
The Radiant Efficiency of Arc Lamps. HENRY PHELPS GAGE 111
The Transmission of Sound Through Porous and Non-porous Materials. C. S. McGINNIS and M. R. HARKINS 128
The Selective Reflection of Ortho-, Meta- and Pyro-phosphates in the Infra-red Spectrum. GRACE LANGFORD 137
New Books 152

CLXXXIV. SEPTEMBER, 1911.

The Terminal Velocity of Fall of Small Spheres in Air at Reduced Pressures. L. W. McKEEHAN 153
Heat of Evaporation of Water. ARTHUR WHITMORE SMITH 173
The Distribution of Current and the Variation of Resistance in Linear Conductors of Square and Rectangular Cross-section when carrying Alternating Currents of High Frequency. HIRAM WHEELER EDWARDS 184
On the Nomenclature of Crystallography. PAUL SAUREL 203
On the Positive Potential of Metals in the Photoelectric Effect and the Determination of the Wave-length Equivalent of Roentgen Rays. JAKOB KUNZ 208
Note on a Variable Low Resistance. J. H. DELLINGER 215

CLXXXV. OCTOBER, 1911.

Some Thermodynamic Properties of Air and of Carbon Dioxide. A. G. WORTHING 217
The Magnetization of Cobalt as a Function of the Temperature and the Determination of its Intrinsic Magnetic Field. W. W. STIFLER 268
The Transverse Thermomagnetic Effect in Nickel and Cobalt. ALPHEUS W. SMITH ... 295
The Distillation of Amalgams and the Purification of Mercury. G. A. HULETT 307
The Exception to Hooke's Law. JULIEN C. SMALLWOOD 317
A Simple Proof of Poynting's Theorem. J. F. H. DOUGLAS 322

CLXXXVI. NOVEMBER, 1911.

An Absolute Determination of the Minimum Ionizing Energy of an Electron, and the Application of the Theory of Ionization by Collision to Mixtures of Gases. EDWIN S. BISHOP 325

Studies in Luminescence. XVI. The Fluorescence and Absorption of Certain Uranyl Salts. EDW. L. NICHOLS and ERNEST MERRITT 354

Determination of Peltier Electromotive Force for Several Metals by Compensation Methods. A. E. CASWELL 379

The Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium. F. C. BROWN 403

Thermal Conductivity at High Temperatures. M. F. ANGELL 421

On the Fatigue of Metals Subjected to Roentgen Radiation, in the Presence of Chemically Active Gases. EDWARD G. RIEMAN 433

New Records of Sound Waves from a Vibrating Flame. JOSEPH G. BROWN 442

Proceedings of the American Physical Society 447

Minutes of the Fifty-eighth Meeting: The Electron Theory of Contact Electromotive Force and of Thermoelectricity, *O. W. Richardson;* The Influence of Contact Difference of Potential on the Measurement of Electron Velocities in the Photoelectric Effect, *Karl T. Compton;* The Positive Ionization from Hot Salts, *O. W. Richardson;* Torsional Rotatory Polarization, *Arthur W. Ewell.*

New Books 452

CLXXXVII. DECEMBER, 1911.

The Optical Constants of Alloys as a Function of Composition. J. T. LITTLETON, JR. 453

The Acoustic Shadow of a Rigid Sphere, with Certain Applications in Architectural Acoustics and Audition. G. W. STEWART 467

Artificial Rotatory Polarization. ARTHUR W. EWELL 480

The Measurement of the Frictional Force Exerted on a Sphere by a Viscous Fluid, when the Center of the Sphere Performs Small Periodic Oscillations Along a Straight Line. GEORGE F. MCEWEN 492

Entladungsstrahlen at Atmospheric Pressure and at Diminished Pressures. ELIZABETH R. LAIRD 512

Note on Electrically Produced Water Ripples. FREDERIC PALMER, JR. 528

The Thermoelectric Behavior of Heusler Alloys in a Magnetic Field. L. O. GRONDAHL and S. KARRER 531

Certain Characteristics of Light-negative Selenium. LILAH B. CRUM 538

Refractive Index of Metals. P. A. ROSS 549

Proceedings of the American Physical Society 557

A New Virial Theorem, *D. F. Comstock;* A New Form of Gold-Leaf Electroscope: A Null Instrument, *J. C. Hubbard;* Spectral Luminosity Curves Determined by the Method of Critical Frequencies, *Herbert E. Ives.*

Errata and Addenda 563

Index 564

Volume XXXIII. *July, 1911.* *Number 1*

THE

PHYSICAL REVIEW.

THE NATURE OF LIGHT ACTION IN SELENIUM.

By F. C. Brown.

IN a paper by Brown and Stebbins[1] it was shown that the light-sensitiveness of a certain selenium cell was a function of its resistance whether that resistance was conditioned by temperature, pressure, light or other agencies. This conclusion, together with the results of recent investigations, has led me to formulate an hypothesis for explaining the changes in the electrical conductivity occurring in light-sensitive selenium. The statement and the discussion of this hypothesis together with the results of investigations pertinent to this hypothesis will form the material of this paper. As the amount of data that must be correlated is quite large indeed, particular attention will be given only to the various effects produced by light.

The hypothesis is that all light-positive and light-negative varieties[2] of selenium consist of various mixtures of three kinds of selenium which we will call A, B and C, and that under the action of light A is changed into B and B is changed into C, according to the reaction,

$$A \rightleftarrows B \rightleftarrows C$$

and that the changes in both directions are proportional at all times to the amounts of the changing material. The principal argument that is offered for proposing such an explanation is that it seems to be consistent with the experimental facts under a variety of conditions, and that as is generally recognized previous theories do not explain many of the recently observed phenomena.

That the effect of illumination on certain varieties of light-positive selenium is to produce a genuine change in the selenium itself has not been questioned since Pfund[1] and Berndt[2] showed that selenium cells made by using selenium of the highest purity and carbon electrodes were sensitive to light. By studying the conductivity at different temperatures Marc[3] concluded that certain varieties of selenium consist of two allotropes A and B in equilibrium. Montén[4] by observing the resistance in the dark at pressures between 0 and 3,000 atmospheres concluded that the selenium cells that he used consisted of at least two allotropes A and B in equilibrium under the given pressures.

---

[1] Phys. Rev., 26, p. 273, 1908.

[2] For the meaning of this terminology see Phys. Rev., XXXII., p. 237, 1911.

More recently Kruyt[5] has made density measurements that indicate that in light-sensitive selenium there are two components that are in equilibrium according to the reaction $A \rightleftarrows B$.

This paper will not attempt to define the three components whose existence is supposed nor will it consider the particular reasons why the components have different rates of change under the same external conditions. But since Biltz and Preuneur[6] have found three components in sulphur changing under the influence of pressure and temperature according to the reaction

$$S_8 \rightleftarrows S_4 \rightleftarrows S_2$$

it would not be surprising to find later that the three components of light-sensitive selenium may be identified and studied as separate allotropic forms.

THEORY.

In order to obtain conditions which are easily subject to theoretical treatment we will suppose that the sensitive layer of selenium may be so thin that the impinging light may be of practically uniform intensity throughout the layer, and that temperature, pressure and all other conditions except that of illumination that affect the conductivity remain constant; further suppose that the conductivity of the A kind is zero, while that of the B kind approaches that of the metals and that the conductivity of the C kind is so much smaller than that of the B kind that it may be neglected. Part of the experimental evidence in favor of neglecting the conductivity of the C kind will be brought out in this paper but the most direct evidence will be presented in a later paper concerning the recovery of selenium. Let α_1 and β_1 be the respective rates of change of A into B and B into C for a given set of conditions and α_2 and β_2 the corresponding reverse changes of C into B and of B into A. Let A_0, B_0 and C_0 represent the initial amounts of the respective kinds before illumination. By illumination the constants α_1 and β_1 increase in value and are probably accompanied by small changes in α_2 and β_2, so that after a time t_1, the respective amounts of the three kinds are A_1, B_1 and C_1. Nothing will be said concerning the homogeneity and uniformity further than that the way in which the three components are mixed shall not to any great extent affect the following expression for the conductivity,

---

[1] Phil. Mag., 7, p. 26, 1904.

[2] Phys. Zeit., 5, p. 121, 1904.

[3] Zeit. anorg. Chem., 48, p. 5, 1906.

[4] Archiv. för Matematik, Astronomi och Fysik, 4, p. 1, 1908, also dissertation on "The Influence of Pressure on the Electrical Resistance of Selenium and Silver Sulphide."

[5] Zeit. für anorg. Chemie, 64, p. 305.

[6] Zeit. Phys. Chem., 39, p. 323.

$$i = K_1 B. \tag{1}$$

Then the changes take place in accordance with the following equations:

$$dA/dt = \alpha_2 B - \alpha_1 A, \tag{2}$$

$$dB/dt = \alpha_1 A - \alpha_2 B + \beta_2 C - \beta_1 B, \tag{3}$$

$$dC/dt = \beta_1 B - \beta_2 C, \tag{4}$$

$$A + B + C = K, \tag{5}$$

$$dA/dt + dB/dt + dC/dt = 0. \tag{6}$$

From these equations we obtain the differential equation,

$$[\ddot{B}] + (\mu + \alpha_1)[\dot{B}] + (\alpha_1\mu - \alpha_2\lambda)B - \beta_2\alpha_1 K = 0, \tag{7}$$

where

$$(\alpha_1 - \beta_1) = \lambda,$$

$$\alpha_2 + \beta_2 + \beta_1 = \mu.$$

This equation is of the form,

$$[\ddot{B}] + M[\dot{B}] + NB - L = 0.$$

The solution of the equation is

$$B = L/N + c_1 e^{+m_1 t} + c_2 e^{m_2 t}, \tag{8}$$

and

$$C = \frac{L\beta_1}{N\beta_2} + \frac{\beta_1 c_1 e^{m_1 t}}{\beta_2 + m_1} + \frac{\beta_1}{\beta_2 + m_2} c_2 e^{m_2 t}, \tag{9}$$

where

$$L = \alpha_1 \beta_2 K, \tag{10}$$

$$N = \alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2, \tag{11}$$

$$m_1 m_2 = \alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2, \tag{12}$$

$$m_1 + m_2 = -(\alpha_1 + \alpha_2 + \beta_1 + \beta_2), \tag{13}$$

$$B_0 = L/N + c_1 + c_2, \tag{14}$$

$$C_0 = L/N \times \beta_1/\beta_2, \tag{15}$$

for equilibrium in the light,

$$B_1 = \frac{L}{N} = \frac{(\alpha_1\beta_2)K}{\alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2}, \tag{16}$$

$$C_1 = \frac{L}{N} \times \frac{\beta_1}{\beta_2} + \frac{\beta_1}{\beta_2 + m_1} c_1 + \frac{\beta_1 c_2}{\beta_2 + m_2}, \tag{17}$$

$$\frac{\alpha_2}{\alpha_1} B_1 + B_1 + \frac{\beta_1}{\beta_2} B_1 = K, \tag{18}$$

and the value of the constants in equation (8) are

$$c_1 = \left[\frac{C_0}{\beta_1} + \left(\frac{L}{N} - B_0\right)\frac{1}{\beta_2 + m_2} - \frac{L}{N\beta_2}\right]\left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_2 - m_1}\right], \tag{19}$$

$$c_2 = \left[\frac{C_0}{\beta_1} + \left(\frac{L}{N} - B_0\right)\frac{1}{\beta_2 + m_1} - \frac{L}{N\beta_2}\right]\left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_1 - m_2}\right]. \tag{20}$$

Since the conductivity depends only on the amount of the B kind present, our problem is to determine how the amount of the B kind should vary with the time of illumination, as specified in equation (8), when different initial conditions are considered. To do this we must first determine the constants m_1 and m_2 and c_1, c_2 and L/N. These constants depend on the rates of change and the initial amounts of the A, B

TABLE I.

Case.	1	2	3	4	5
After illumination α_1	.13	.13	.03	10	10
α_2	10.	10.	.40	.13	.13
β_1	2.66	2.66	.40	2.66	2.66
β_2	.05	.05	.3	.05	.05
m_1	-10.39	-10.39	$-.7$	-2.65	-2.65
m_2	$-.058$	$-.058$	$-.2$	-10.19	-10.19
A_0	14,890.	121,000.	290.	12,880.	2,220.
B_0	1.0	1.0	10.	10,000.	10,000.
C_0	1.0	10,000.	10.	85,120.	95,760.
A_1	9,320.	77,000.	265.	30.	30.
B_1	120.	1,000.	20.	2,000.	2,000.
C_1	6,360.	53,000.	25.	106,000.	106,000.
K	15,900.	131,000.	310.	108,000.	108,000.
L/N	120.	1,000.	20.	2,000.	2,000.
Per cent. A_0	90.	92.	90.	12.	2.
Per cent. B_0	.06	.008	3.2	9.0	9.0
Per cent. C_0	10.	8.	7.	79.	89.0
Before exposure α_1/α_2	$.67 \times 10^{-4}$	8×10^{-5}	.035	.8	5.0
β_1/β_2	1.0	10^{8}	1.0	8.5	9.5
After exposure α_1/α_2	.013	.013	.075	77.	77.
β_1/β_2	50.	50.	1.2	53.	53.

and C components. The rates of change must be positive quantities under all conditions. In accordance with equations (12) and (13) this obviously requires that m_1 and m_2 shall always be of negative sign. Also the amount of the three components A, B and C must necessarily be positive quantities, and it seems reasonable to expect that the ratios α_1/α_2 and β_1/β_2 should always be increased by the action of light. This last presumption would further require that during illumination the amount of the C kind must always be increased and that at the same time the A kind must be decreasing. The B kind may obviously either increase or decrease depending upon the relative amounts of change in the A and C kinds. These are all the conditions that it seems wise to impose at present. Further experimentation may show that not only do the rates of change vary according to simple laws with changes in the intensity but that the ratios of the rates also vary according to correspondingly simple laws.

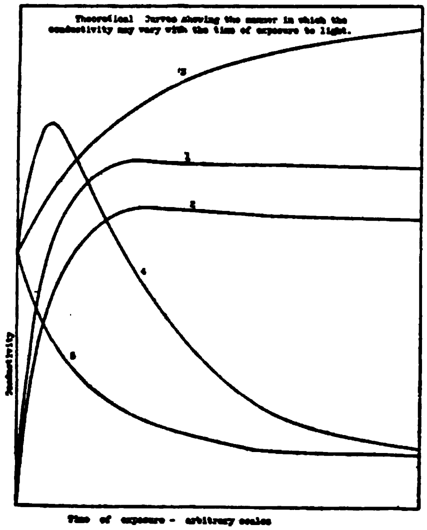


Fig. 1.

By a method of approximations and guesses I have found specimen arbitrary values for the rates of change, which when taken with appropriate values of the other constants will establish the characteristic ways in which the conductivity, i, will vary with the time of exposure to light. All the constants must be in harmony with the twenty equations given and also must satisfy the other necessary conditions. The equation as obtained from (1) and (8) shows the relation between the conductivity and the time of exposure to be

$$i = K_1(L/N + c_1e^{m_1t} + c_2e^{m_2t}). \quad (21)$$

Certain values of the constants and other information is given in the accompanying Table I. This table furnishes the values for the constants in the above equation, the graphs of which are shown in Fig. 1. The equations of the curves are as follows;

curve 1, $B = 120 - 138e^{-10.39t} + 19e^{-.058t}$,
curve 2, $B = 1000 - 1160e^{-10.39t} + 160e^{-.058t}$,
curve 3, $B = 20 - 4.872e^{-.7t} - 5.12e^{-.2t}$,
curve 4, $B = 2000 - 3250e^{-10.59t} + 11250e^{-2.65t}$,
curve 5, $B = 2000 + 5670e^{-2.65} + 2340e^{-10.59t}$.

The main points that are essential to the theory may be understood most easily by studying the curves. In (1) and (2) the initial conductivity is very small and it rises rapidly to a maximum and then falls off slowly to a constant limiting value. The equilibrium value of the conductivity in the light to that in the dark is of the ratio 1,000 to 1. Curve (3) shows the conductivity in the dark to be greater than that shown in (1) and (2). The increase of conductivity due to illumination is always positive. It increases most rapidly at first. In the fourth case the conductivity rises rapidly by illumination to a maximum, that is, relatively to the initial conductivity not very large and then falls off quite rapidly to a value which may be even less than the initial conductivity. Curve (4) shows the manner of variation although it does not show the fact that the initial conductivity is much larger than prevails in the first three cases.

In what is called case 5 the conductivity begins to decrease at once when the light acts on the selenium and it falls rapidly compared to the rate of decrease in the other four cases noted.

Considerable importance is attached to the fact that the decrease of resistance becomes more and more rapid as the conditions change from those required in case 1 on down to those required by case 5, and that in all the cases except No. 5 there are changes in the conductivity in both directions shown in an unmistakable manner; also to the fact that as we shift from cases 1 to 5 the initial or dark conductivity increases.

Case 2 is regarded as a highly improbable one in that the rates of change between *B* and *C* compared to the reverse changes between *C* and *B* are greater before illumination than afterwards.

The theory proposed is simple and attractive in so much as it rather implies that all the agencies that affect the conductivity of selenium produce the same kind of a change in the selenium, namely a variation in the rates of interchange. Or stated in other words the selenium is in equilibrium under a variety of conditions. Each agency merely acts in a way to alter the equilibrium by changing the rates. Whether or not every agency changes the rates in accordance with the same laws after the units have been properly adjusted is a matter that will have to be determined by experiment. Any variety of selenium which shows a marked increase of conductivity at first and then is followed by a decrease when acted on by light should in all probability show the same two changes when acted on by other agencies, but this conclusion is clearly not required. For example, a Giltay or a high sensibility selenium cell which by illumination rises to a maximum conductivity, say 100 times as great haste conductivity in the dark, and then falls to only 30 times the dark conductivity, might reasonably be expected to rise to the same maximum and then to fall to the same limiting value 30 to 1, if there were a sudden application of mechanical pressure of the right amount. The same argument would apply to the agencies of temperature and differences of electric potential.

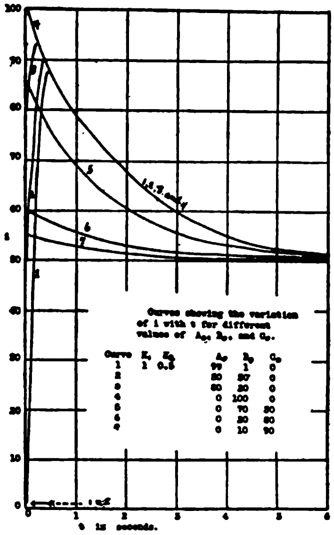
A mechanical interpretation of the theory may be proposed as follows: The *A*, *B* and *C* varieties because of their rates of interchange are in equilibrium. When the selenium is illuminated new rates are established and consequently new equilibrium values for the amounts of the *A*, *B* and *C* kinds. We may regard the selenium as distorted from its equilibrium condition, and the study of the change of conductivity as merely a study of one of the processes taking place while the new equilibrium is being established. In fact experiment shows that it is possible to distort the selenium system, if it may be called such, so that the amount of any kind may be either greater or less than is required for equilibrium. So far as the *B* kind is concerned the distortion may be either positive or negative in at least one variety of selenium, while the condition of light or darkness is changing in only one direction. Or suppose any variety of selenium in equilibrium in the diffuse light of a room; the selenium may be distorted in one direction by imposing the condition of darkness. It may be distorted in the opposite direction by imposing the condition of intense illumination. By increasing the intensity of illumination the amount of the *C* kind increases and by decreasing the illumination the amount of the *C* kind decreases. The following argument will illustrate what general behavior is expected. Suppose a selenium cell in equilibrium in the dark in a condition which we will call ϕ. Next expose it to intense light and as a result of the existing distortion it changes according to certain laws toward a new equilibrium condition which we may call θ. The changes can be shown by curves. Finally remove the selenium to the dark and again due to the distorted condition of the selenium it will return to its former dark condition ϕ. The changes from θ to ϕ can also be represented on curves. The general movement of the change in the first case may be said to be in the positive direction and in the second case it may be said to be in the negative direction. The changes in the negative direction as shown by the second set of curves may be said to be the reciprocal of the changes in the positive direction and the time taken for the selenium to go from θ to ϕ should be of the same order of magnitude as the time required for the selenium to go from ϕ to θ. Where there is a rapid change and a slow change going in one direction there should in general be both the rapid and the slow changes in the reverse process.

In a recent paper[1] given before the American Physical Society was developed an equation for the conductivity on the assumption that the reverse changes α_2 and β_2 were at all times small compared to the direct changes, and that the conductivity of the C kind was one half as large as that of the B kind. It was stated that these assumptions were only tentative. As certain facts are brought out both by the agreement and by the disagreement of the experimental results with the equation developed,

$$i = k_1\left\{\frac{A_0\alpha_1}{\alpha_1-\beta_1}(e^{-\beta_1 t}-e^{-\alpha_1 t})+B_0e^{-\beta_1 t}\right\}$$

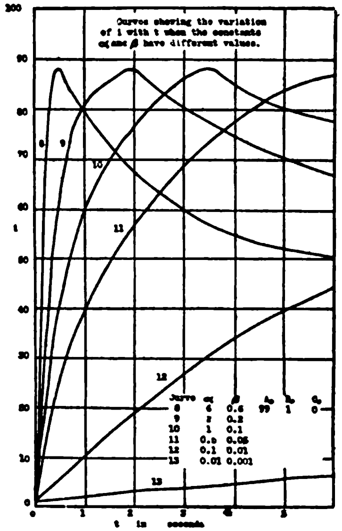
$$+\,k_2\left\{\frac{A_0}{\alpha_1-\beta_1}[\alpha(1-e^{-\beta t}-\beta(1-e^{-\alpha t})]+B_0(1-e^{-\beta_1 t})+C_0\right\}$$

two families of curves taken from this equation are shown in Fig. 2 and Fig. 3. The theoretical objection that is urged against these special assumptions is that there is no method of accounting for the initial amounts of the three kinds in the dark, and consequently no satisfactory way of explaining the recovery of the selenium after the light is removed. Wherein the experimental results show that the special assumptions are not warranted will be brought out in the discussion of the results.



Curve	K_1	K_2	A_0	B_0	C_0
1	1	0.5	99	1	0
2			50	50	0
3			80	20	0
4			0	100	0
5			0	70	30
6			0	20	80
7			0	10	90

Fig. 2.



Curve	α	β	A_0	B_0	C_0
8	6	0.6	99	1	0
9	2	0.2			
10	1	0.1			
11	0.5	0.05			
12	0.1	0.01			
13	0.01	0.001			

Fig. 3.

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[1] PHYS. REV., Vol. XXXII., p. 237, 1911.

GENERAL CONSIDERATIONS.

Some time ago I observed a striking relation between the resistance of selenium and its sensibility to light. In this instance, sensibility is used in the sense of the ratio of the conductivity in the light to the conductivity in the dark, when the selenium was exposed directly to sunlight or its equivalent for about 5 minutes. The relation observed was that the higher the resistance the greater was the sensibility or conversely the lower the resistance the less the sensibility and finally when the resistance became very low the sensibility became of the negative sign. The accompanying Table II. shows the observations that were made. However it must be remembered that the values represent only orders of magnitude. The specific resistance is not in all cases proportional to the measured resistance of the selenium. Further as the sensibility was measured without any intention of making such comparisons as here noted, the sensibility also is subject to a large error. Nevertheless the relation mentioned is very clearly shown.

TABLE II.

Kind of Selenium.	Resistance.	Sensibility.
High sensibility selenium cell,	10^9	200 to 1
Giltay selenium cell,	400,000	30 to 1
Ruhmer selenium cell,	90,000	10 to 1
Home made, 1904,	100,000	10 to 1
Home made, 1904	160,000	4 to 1
Home made, 1904,	30,000	2 to 1
Home made, 1904,	17,000	1.1 to 1
Home made, 1904,	12,000	1.0 to 1
Home made, 1904,	3,500	1.0 to 1
Light negative selenium,	400	−1.002 to 1
Light negative selenium,	20	−1.15 to 1
Light negative selenium,	1	−1.5 to 1

Since making these observations I have learned that Pochettino and Trabacchi[1] and also J. W. Giltay have made observations that show this same relation existing between resistance and sensibility. Giltay in one of his trade circulars on selenium cells, says that he makes high resistance selenium cells of high sensibility and low resistance selenium cells of low sensibility and adds that "low resistance and high sensibility simply do not go together."

As an example of diverse facts concerning selenium, which do not seem to any conclusion we may note the laws of change of conductivity with light intensity as given in Table III., where *m* represents the change of conductivity, i represents the light intensity, R the resistance, and the other quantities constants.

---

[1] According to Ries in his book on Die Elektrischen Eigenschaften und die Bedeutung des Selens für die Electrotechnik.

TABLE III.

Law.	Authority.
$i = cm^2$	Rosse, Adams, Berndt.
$i = cm^3$	Hopius.
$i = m(m-a)b$	Athanasiadis.
$i = b^m - 1$	Hesehus.
$R_a/R_b = (b/a)^a$	Ruhmer.
$I = cm$	Stebbins.[1]

Without doubt all the variations in the results of the above investigators can be explained on the ground that the conditions were widely different in many cases. The varieties of selenium were not the same; the intensity ranged between different limits; and no doubt the time of exposure was different in each case. Other legitimate reasons might be sought for in the construction of the cell form and the thickness of the selenium on this form. The facts in this table are presented merely to demonstrate the futility of search for a simple universal law connecting the conductivity of a selenium cell and the intensity of illumination. It is obviously necessary to look to other relationships than the one mentioned if we wish to connect the facts by simple laws.

The properties of the known varieties of selenium are summed up in Table IV., so far as information has been obtained. The purpose here is to call attention in a more general way more particularly to the diverse properties of selenium.

TABLE IV.

Variety of Selenium.	Change of Conductivity by Light.	Conductivity in the Dark.	Direction of Change of Conductivity.			
			By Temperatures.	By Pressure.	By Electrical Diff. Potential.	By Moisture.
High sensibility cell....	+ followed by −	10^{-9}	−	?	+	+
Giltay cell............	+ followed by −	10^{-6}	+	+	+	?
Ruhmer cell...........	+	10^{-5}	+	+	+	+
Ries's "abnormal cell"..	+ followed by −	?	?	?	?	+
Light-negative cell.....	−	10^{-2}	+	?	+ or −	−

It is not certain how many of these diverse properties may be in part due to impurities in the selenium. Also we are very much in doubt as to what is the depth of penetration of selenium by light. Before the proposed theory can be put to a rigid test it will be necessary to answer the last question but not the first. But this question cannot be answered at present. We may now proceed to call attention to experiments with the above varieties of selenium.

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[1] Proved by Stebbins for faint illumination by two independent methods in connection with his work on the Measurement of the Light of Stars by a Selenium Photometer, in Astro-Phys. Jour., 32, p. 185, 1910. However his results are not published.

EXPERIMENTS WITH LIGHT-POSITIVE SELENIUM.

In most of the experiments with light-positive selenium, a selenium cell designated Giltay No. 2, which was made by Giltay of Delft, Holland, was used. For somewhat more than a year previous to its use for the experiments described in this paper it has been left in paraffin oil in a glass tube of about 4.5 cm. diameter and 25 cm. length. With the exception of a space left for a window, the tube had been black enameled on the exterior surface. This tube was surrounded by a second similar tube. When the second tube was so turned that the two windows were together, the cell could be illuminated. The temperature of the oil in which the cell was placed was read from a thermometer projecting through a rubber cork down into the oil. In the dark at 25° C. the cell had a resistance of about 490,000 ohms.

Whenever changes in the conductivity were investigated that occurred during short intervals of time, a pendulum and a ballistic galvanometer were used in connection with a Wheatstone's bridge circuit. This method of measuring such changes of resistance is discussed elsewhere.[1] It will be sufficient to state here that the average conductivity of the selenium during any interval is a function of the deflection of the galvanometer, which function can be determined either by experiment or calculation. The method of illumination was to place a tungsten lamp in the same dark box in which the selenium cell was placed and to regulate the time of illumination by opening and closing keys controlling the current through the lamp. If the period of illumination desired was a fraction of a second, the keys were manipulated entirely by the pendulum which threw in the ballistic galvanometer. It was assumed that the light reached a constant value at once and no correction was made for the fact that the candle-power of a tungsten lamp decreases perceptibly after the current is turned on.

The change of conductivity varies with the time of illumination. In all high sensibility selenium cells the conductivity first rises rapidly to a maximum and then it falls off fairly rapidly at first and then more slowly. This is shown for the Giltay No. 2 in curve 14 of Fig. 4, where the cell was exposed to a 16-cp. lamp at about a distance of a meter.

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[1] See paper by Brown and Clark, PHYS. REV., 1911.

The maximum conductivity is reached in about 50 sec. and is about seven times greater than the conductivity in the dark. In curve 15 is shown the variation of conductivity with time for a very intense illumination. The intensity was approximately that of a 32-cp. lamp at a distance of 7 cm. It will be noted that the maximum conductivity is reached in .35 sec.

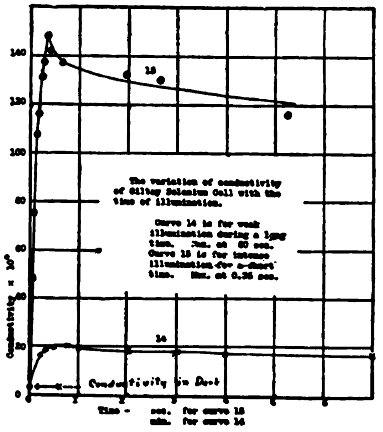

Fig. 4.

A fair sample of the observations taken to obtain the data for such a curve is given in the following Table V. The first key closes the storage battery circuit through a tungsten lamp. The second key throws the ballistic galvanometer in circuit and the third key again opens the galvanometer circuit.

There are three sources of error in obtaining these observations which for our present considerations are of minor importance. The first arises from the fact that the intensity of illumination of a tungsten lamp does not become constant at once when the current is turned on. The second error was in the current itself. The storage battery used did not

Table V.

Observations on the Change of Conductivity of Selenium Cell Giltay No. 2 with Time by Use of Pendulum and Ballistic Galvanometer.

Temp.	Resistance in Dark.	Distance Apart of Second and Third Keys.	Time of Exposure.	Mean Corrected Time.	Deflection.	Conductivity ×10⁸.
			0	0	0	2.7
28° C.	370,000	.1 sec.	0.1 sec.	0.050	28	48
		.05	0.1	0.075	35	75
		.05	0.15	0.125	41	107
		.05	0.2	0.175	45.5	116
		.05	0.25	0.225	50.8	131
		.05	0.30	0.275	52.5	137
		.05	0.35	0.325	56.5	148
		.05	0.40	0.375	52.5	137
		.05	0.40	0.375	53.1	141
		.05	0.65	0.625	52.4	137
		.05	2.65	2.62	48.9	130
		.05	2.0	1.97	48.1	129
		.05	5.25	5.22	45.0	115
		.05	9.4	9.4	41.	107

furnish an unvarying E.M.F. After a few seconds use there was observed several times a slight decrease in the current. If however the lamp was connected in the regular lighting circuit substantially the same results were obtained as when the storage battery was used. The third error arose from incomplete recovery between readings. Practically from 1 minute to 1 hour was considered sufficient time, the time depending upon the intensity and duration of exposure and the temperature. For reasons which will be given later, we shall see that the reaching of the initial dark resistance does not necessarily require that the equilibrium condition shall be reached for a particular temperature or light condition. But equilibrium does require a particular resistance, under given conditions.

The amount of the decrease of conductivity in the Giltay cell is by no means pictured in curve 15. Other sets of observations were made where the time of illumination extended over a period of 15 minutes, *i. e.*, about one hundred and fifty times as long as in the instance just discussed. A Siemens and Halske needle galvanometer was placed in series with the cell and the conductivity was determined directly from the readings. The intensity of illumination was approximately the same as that for the short exposure. The decrease of the conductivity was extremely large as will be readily seen by referring to curves 16 and 17 of Fig. 5. In these cases the maximum conductivity was probably reached in 0.4 sec. At the temperature of 17° C. the conductivity was of the order of one hundred times that of the conductivity in the dark and at 41° C., the maximum ratio of the two conductivities was about 30 to 1. It may be observed from the curves that these ratios decreased after 10 minute exposures to 60 to 1 and 12 to 1. These last ratios probably represent very nearly the condition of equilibrium with the given intensity of light compared with equilibrium in the dark for the two temperatures stated. It is significant however that the equilibrium is approached with equilibrium in the dark for the two temperatures decidedly more rapidly at the higher temperature. The first deflection of 40 recorded in curve 17 is no doubt somewhat too high, due to the inertia of the galvanometer needle system.

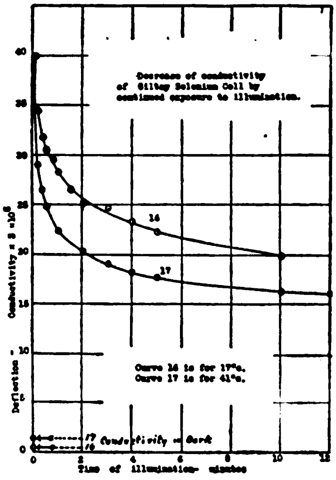

Fig. 5.

The remarkable decrease in the conductivity of the Giltay cell is just as remarkable as is the enormous increase at first. Certainly it is of just as much importance theoretically. First of all it is quite necessary to know if this decrease in the conductivity represents a genuine change in the selenium or if it is a polarization phenomenon. This question is a particularly legitimate one in view of the fact that many selenium cells show extreme polarization under the action of light and the electric current. I wish to state at the outset that none of the phenomena I have observed recently in light-positive and light-negative selenium arise from polarization by the current. My reasons for making such deductions with regard to the Giltay cell are as follows:

(*a*) First the selenium cell was balanced in a Wheatstone's bridge circuit after being intensely illuminated for several minutes. Then the battery circuit was broken. There was not the slighest deflection of the galvanometer by this procedure. This showed that no appreciable back E.M.F. was produced by the combined actions of the light and the electric current.

(*b*) Again the cell was connected in one arm of the bridge illuminated and balanced. The battery current was then quickly reversed by a reversing key. There was no apparent change of resistance. If there had been any polarization practically its whole effect would have had to disappear in less than a second. This might have been regarded as sufficient proof of the non-existence of polarization. (*c*) Next a test was made to see if the decrease of conductivity in the Giltay cell took place independent of the action of the current during the period of illumination. It was found, for example, that the conductivity at any time after the cell had been illuminated for 2 min. 10 sec. was that shown in curve 17 whether the current was flowing through the cell during the first two minutes or not.

At another time two series of observations were taken, one with the current acting all the time and the other with the current off during the first 60 seconds. The results are shown in the following table, where the conductivity in the dark is represented by unity, and where the observations were taken in the order enumerated by the sets.

Remembering that the current flowing through the selenium cell when the above observations were made was from 20 to 100 times larger than it was during the previous observations when the pronounced decrease of conductivity in the Giltay cell by light was noted, and allowing for the inconstancy of the light source, it may be concluded that the light action is independent of the current.

(*d*) Fearing that some might raise the question as to whether the 10 seconds allowed for the resistance determination might not be sufficient time for the current to produce the decrease under discussion, a further

TABLE VI.

Conductivity of Selenium Cell after Being Exposed to Light.

Time of Exposure.	Conductivity without Current Flowing in Cell. Av. of Sets II. and IV.	Conductivity with Current Flowing in Cell. Sets III.
70 sec.	32.7	32.3
90 sec.	31.9	31.2
2 min.	30.7	30.3
	Set IV.	Av. of Sets III. and V.
70 sec.	30.5	30.7
90 sec.	29.9	30.0
2 min.	29.2	29.1
	Av. of Sets I. and III.	Sets II.
90 sec.	34.1	33.2
2 min.	32.9	32.2

test was made in which the mean time that the current flowed through the cell was 0.06 second. The pendulum before mentioned in this paper was used to first close the battery circuit for lighting the tungsten lamp when desired, then to close the battery circuit through the selenium cell and Wheatsonte bridge circuit, and 0.01 sec. later to close the galvanometer circuit for a period of 0.1 sec. The resistance of the cell was 640,000 ohms and the fall of potential across it was about 0.1 volt. The following are the observations:

Time of Exposure, Seconds.	Deflection without Current Acting.	Deflection with Current Acting.
0.5	43.0	43.3
1.5	67.5	66.9
2.5	68.8	66.9
3.5	70.1	—
5.5	66.9	67.5
10.5	64.9	65.3 and 63.2

As in the previous observations the conductivity is a function of the deflection. The slight differences in the deflections with and without the current acting can be explained by assuming that the selenium had not recovered by the same amount for all the observations.

It may now be considered definitely settled that the decrease as well as the increase of conductivity in the Giltay selenium cell no. 2 represents a genuine change in the selenium or what is supposed to be selenium and not what is ordinarily termed polarization.

It has been shown by a great many investigators that the sensitiveness of selenium decreases with increase of temperature. However it has not been shown to my knowledge how the conductivity for different times of exposure varies with the temperature. As questions in the theory are involved in such information, I have obtained data at different temperatures for time conductivity curves. Such curves are shown in Fig. 6. While the observations are not very accurate, and the range of temperature is not very great, yet it is safe to draw certain conclusions. The conductivity in the dark is more than four times larger at 46.5° C. than it is at 11° C., and yet the maximum conductivity under the influence of intense illumination has nearly the same value. This is of course in agreement with the well established fact that the sensibility of certain selenium cells decreases greatly with rise in temperature. The maximum

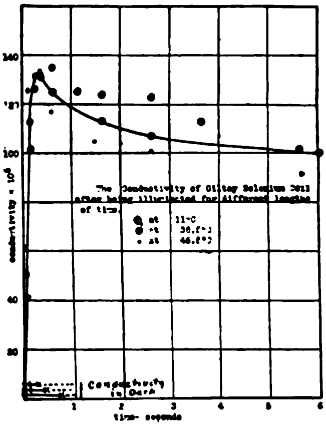

Fig. 6.

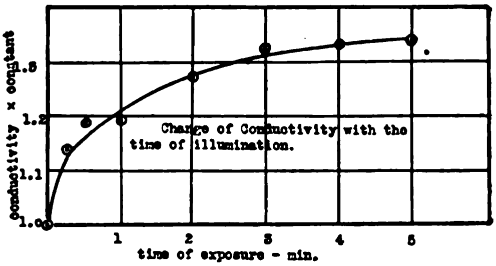

Fig. 7.

seems to be shifted toward the conductivity axis at higher temperatures. However there is reason for believing that the intensity of illumination was slightly less at the higher temperature than at 11° C.

Another class of light-positive selenium continues to increase in conductivity when it is illuminated. The selenium in the Bidwell and also the Ruhmer cells belong to this class. In Fig. 7 is shown how the conductivity varies with the time of exposure for a selenium cell of the Bidwell type. In this particular cell the resistance was only 8,000 ohms, and the sensibility was very low. The cell was not surrounded by a liquid while the readings were being taken; consequently a part of the observed change of conductivity may have been due to temperature. In Fig. 8 are shown similar curves for two other cells of this class.[1] Curve *I* is for a cell that was slowly cooled in the making process, and curve *II* is for one that was quickly cooled in

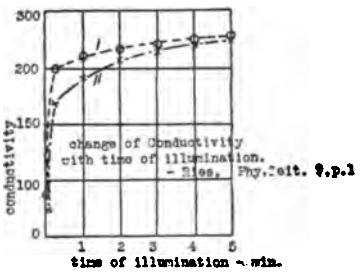

Fig. 8.

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[1] These are taken from a paper by Ries, Phys. Zeit., 9, p. 9, 1908.

the making. He does not state the resistance of the cells or what was the intensity of illumination. For the cell referred to in Fig. 7, the intensity was that of a 16-cp. lamp at a distance 20 cm. When the intensity was greater than this the rise of the conductivity was more rapid at first and the final value was somewhat larger. In fact any light-positive selenium shows that the equilibrium value of the conductivity to increase with the intensity of illumination. Whether this equilibrium value varies in the same manner as does the conductivity for a very short period of illumination has not been investigated. Aside from the manner in which the "conductivity-time of exposure" curves differ in the two classes of selenium, there are two additional characteristic differences. The sensibility is much lower in the second class and the initial dark resistance is lower. At this time no special importance can be attached to the fact that the changes take place more slowly in the second class than in the first. The depth of the selenium and the intensity of illumination should be alike in order that such comparisons should be of particular value.

EXPERIMENTS WITH LIGHT-NEGATIVE SELENIUM.

Because of the difficulty of manufacture of selenium that decreases its conductivity upon exposure to light, I have not been able yet to determine the exact treatment of selenium that produces this so-called light-negative variety. In fact it took just as long and just as much patience to make the fifth sample as it did the first one. We shall therefore confine our attention to an analytical study of the behavior of these samples, particularly under the influence of light.

The general characteristics of this variety are not rigidly defined, except on a few points. The resistance is always small, and when the sample is first prepared it is very unstable. The smaller the resistance the greater is the sensibility, *i. e.*, the greater is the percentage change of resistance by light. Usually the amount of decrease of conductivity increases with increased illumination, but many times I have observed that a weak illumination such as the diffuse light of the room produces practically as great a change as does an intensity one hundred times as great. Generally the selenium recovers quickly when the light is removed, but after many exposures it may become fatigued and not recover for hours or at all. If the recovery is only partial then the sensibility is reduced. A few times and without any warning the selenium has for a single exposure become light-positive instead of light-negative. This was usually when the resistance was unsteady and when the selenium had been repeatedly illuminated. With one exception this reversal of effect has occurred only in newly prepared samples.

The following table will show the regularity of the increase of resistance of two samples which were about a year old. Unless otherwise specified the illumination was quite intense.

Table VII.

Table Showing by Successive Readings the Decrease of Conductivity in Two Samples of Light-Negative Selenium.

Sample No. 9. Time of Observation.	Resistance in Ohms. In Dark.	In Light.
3:09	107	107.2 in diffuse light.
3:14	107.6	108.6 intense illumination.
3:17	107.6	108.6
3:25	107.6	108.4
3:32	107.6	108.7
3:54	107.6	108.7
4:06	107.65	108.7
4:21	107.6	

No. 2.

In Dark.	In Light.
18.9	22.8 in diffuse light.
21.8	24.0 in diffuse light.
22.0	24.7 in diffuse light.
	25.2 20 cm. from 16-cp. lamp.
22.7	23.2 20 cm. from 16-cp. lamp.

When first made these samples showed the same amount of increase usually, but not only did the resistance in the dark shift very suddenly and irregularly, but the amount of the change in the light was very irregular and at times zero. The irregularities were made more pronounced by sudden changes of temperature or by very intense illumination. Table VIII. shows how the resistance gradually increased as the temperature was successively changed.

Table VIII.

Resistance in Dark, Ohms.	Temperature, Degrees Cent.
117	20
123	5
153.5	−10
148	0
157	20
191	3
189	4.5
196	−7
190	2
181	8
167	20
154	39
183	45

From this table it is observed that the general tendency is for the resistance to decrease by raising the temperature and for it to increase by lowering the temperature, but that the net result is an increase of resistance. Not only is the process not a reversible one, but often a change of temperature in either direction increases the resistance. The irregularities were exaggerated by extreme or rapid changes of temperature. All that has just been said however applies only to samples that have been newly made. The increase of resistance of sample no. 1 at the above temperatures was of the order of 1 ohm. By suddenly changing the temperature up and down as indicated in the above table and by tapping the selenium with a thermometer the resistance was further increased to 481 ohms at 24° C. It was then exposed to the light of a well lighted room for several months during the summer. All the time it was immersed in paraffin oil in a similar manner to that described previously as in use for the Giltay cell. At the end of the summer the selenium had increased in resistance to 6,200 ohms and it was not measurably sensitive to light. But this was not the most surprising thing. After being removed to the dark for a period of about a month its resistance fell back to 675 ohms, where it was somewhat unsteady and after the current was allowed to flow through it for an hour it fell still further to 67 ohms. It was then light-sensitive as before and has remained so for several months.

The way that the conductivity of these light-negative samples vary with the time of exposure is shown in Fig. 9. The lower curve is for sample no. 9, which had a resistance of 107 ohms. The resistance of this sample was perhaps the most steady at all times of any that I have made. The upper curve applies to sample no. 10, which had a resistance of 312 ohms. It should be noted that almost all of the change takes place in less than a second. The intensity of the light was not much different from that used on the light-positive selenium which gave the results show in curves 15, 16 and 17. The rate of decrease in the latter

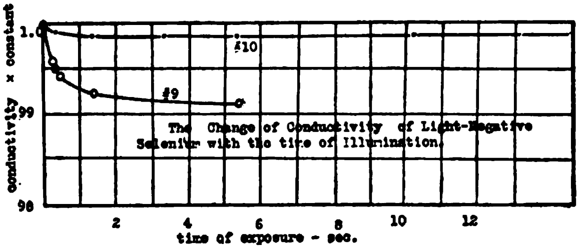

Fig. 9.

case is about 200 times greater than it is in the Giltay cell. Further experiments should be carried on with this light-negative variety, in order to determine the conditions of stability and instability.

RIES'S "ABNORMAL SELENIUM CELLS."

Ries in his paper on the "Effect of Moisture on the Electrical Properties of Selenium"[1] discusses a most peculiar variety of selenium which he has produced. When illuminated these abnormal selenium cells first rise to a maximum very quickly and then fall off slowly to a minimum value, very much as noted for the Giltay selenium cell. Sometimes the conductivity would even decrease below the conductivity in the dark. Two of his curves are shown in Fig. 10. The conductivity of these samples never increased much above that of the dark conductivity. The initial resistance and the intensity of illumination are not stated. He regards the decrease of resistance as a spurious effect which merely counteracts the positive light-action. His experiments indicate that moisture plays an important part in the formation and persistence of this variety. I have not yet succeeded in reproducing his so-called "abnormal selenium cells," but this is no doubt because I have not duplicated the exact necessary conditions. I should prefer however to call this variety a third or modified type of the light-positive variety.

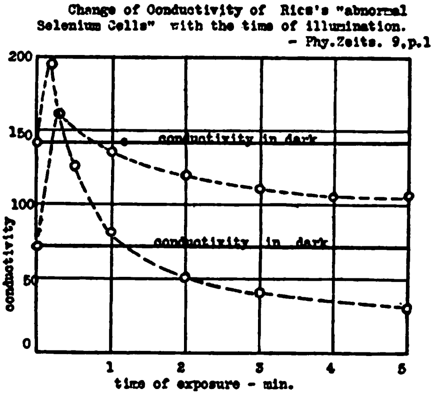

Fig. 10.

THE APPARENT FAILURE OF OHM'S LAW.

Ohm's law states that in an electrical conductor the current flowing is proportional to the difference of potential, assuming of course that all other conditions remain fixed. In all varieties of light-sensitive selenium this law apparently does not hold. As the voltage across the selenium is increased the current usually increases at a more rapid rate than it should. The amount of the change in the specific conductivity is sometimes very large. The curves in Fig. 11 show how the variation differs in the two classes of light-positive selenium. It is noted that in the Ruhmer cell the amount of variation is almost proportional to the voltage, while in the Giltay cell the variation decreases as the voltage is increased. The different high potentials were applied from 20 seconds to 1 minute before each observation was taken. It was suspected that the falling off of the effect in the Giltay cell was due to a decrease of the conductivity by the high potential much the same as is produced by light. This suspicion was strengthened by leaving the potential of 116 volts on the cell about a minute before taking the observation. It is seen that this point is below the curve. In other words, just as in the case of light the change of conductivity is a function of the time of application of the changing agent. The way that the decrease takes place is shown by the observations recorded in Fig. 12. This curve tells its own story when it is compared with the curves 16 and 17 in Fig. 5. There can be little doubt but that just as light produces a rapid change in the positive direction followed by a slow change in the negative direction, so are there corresponding changes produced by difference of electrical potential. In order to be certain that

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[1] Phys. Zeit., 9, p. 1.

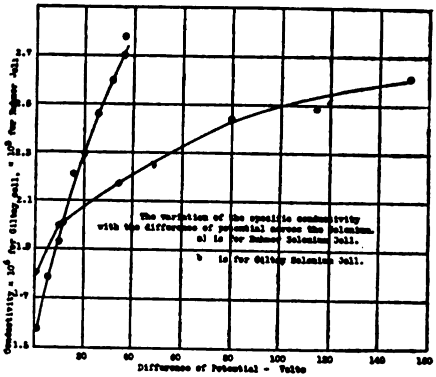

Fig. 11.

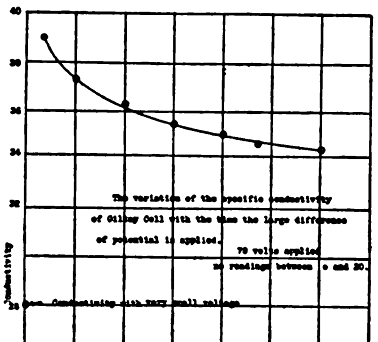

Fig. 12.

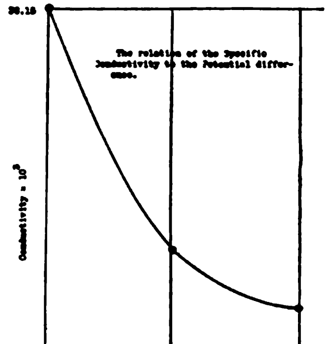

Fig. 13.

the variation first increased rapidly and then decreased slowly, the pendulum and ballistic galvanometer previously referred to were used. First the selenium cell was balanced in the Wheatstones bridge circuit where the fall of potential was two volts. Then the pendulum was arranged to throw 120 volts instead of the 2 volts into the circuit for varying intervals of time. The galvanometer was in circuit during the last 0.1 sec. of the intervals. The deflection was a function of the change of resistance as usual. The relation of the change of resistance to the deflection may be estimated from the following:

$\Delta x = 600{,}000$ ohms, $d = 3.5$ mm.
$\Delta x = 650{,}000$ ohms, $d = 5.3$ mm.
$\Delta x = 700{,}000$ ohms, $d = 23.5$ mm.

The following table, IX., shows that the maximum conductivity was reached in about 0.1 sec. The increase is rapid and large in amount and the decrease is small and slow in taking place.

TABLE IX.

Time of Application.	Deflection, mm.	Time of Application.	Deflection, mm.
.01 sec.	1.0	.10 sec.	27.3
.02	5.0	.10	26.0
.05	10.9	.20	24.2
.01	1.5	.50	22.5
.02	2.5	7.0	3.5
.02	5.0	10.0	2.7
.01	1.2	60.0	2.5
.05	22.5	60.0	2.0
.10	27.1		

The variation of the specific conductivity of light-negative selenium takes place within quite a different range of potentials than it does for the light-positive selenium. Between two and ten volts I could not detect any variation whatever with certainty. But between 0.001 and 2.0 volts the effect of the variation of the potential difference was unquestionable. The curve in Fig. 9 shows the effect of varying the voltage on light-negative no. 9. The readings were taken after the potential had been applied about a minute. There was evidence that the change was a function of the time also. However this change was so small that it could not be clearly distinguished from a possible temperature effect. The important conclusion is that the electrical difference of potential changes the specific conductivity and in the same direction as the change by light. I have one low resistance sample of selenium that continues to show the light-positive characteristics at times. Also its specific conductivity increases with increase of voltage. Further experiments must be carried on with this sample.

DISCUSSION OF RESULTS.

On the basis of our explanation we have deduced four particular characteristic equations, which show the relations existing between the time of exposure and the conductivity. These relations are shown in the curves in Fig. 1. Experimental results bearing on these relations with all the known varieties of selenium are recorded. The thickness of the selenium varied between 0.1 mm. and 1 mm. While the thicknesses are unquestionably greater than is permitted by the theory because of the absorption of light by selenium, nevertheless it seems that the general form of the conductivity-time curves should not be materially different from what it would be if the layer were very thin. Experiments have not yet been completed for the determination of the depth of penetration of selenium by light, but the indication is that the light penetrates much deeper than is generally supposed, particularly in the light-positive varieties.

The results showed, that the Giltay cell gave curves very similar to 1 and 2, that the cells of the Bidwell type gave data for a curve like no. 3, that the light-negative selenium led to curves of the character of no. 5, and that Ries's "abnormal selenium cells" led to a curve like no. 4. I may state that I found data for curves of no other character to be obtained, either from the theory or from any variety of selenium that has come to my notice. I regard the striking similarity between these experimental and theoretical curves as important evidence in favor of the proposed theory. It seems a waste of time to try to fit the comparison curves more accurately until further information is obtained concerning the depth of penetration of selenium by light.

The curves in Fig. 4 show that with increased intensity of illumination the maximum conductivity occurs sooner, that the maximum is much greater, and that the equilibrium value of the conductivity is correspondingly greater. Any view of the theory requires that the rates of change shall be a function of the light intensity. The curves in Fig. 3 show how the maximum should be shifted if the reverse changes were small in comparison with the direct changes. The form of the curves agrees with the experimental curves, and the maximum occurs quicker with increased intensity. Also for faint illumination the change of conductivity is almost proportional to the time of exposure. This agrees with the relation of the conductivity to the time of exposure as determined by Stebbins. But there is disagreement on two fundamental points, viz., this assumption will not account for the different values of the maximum conductivity or for the different values of the equilibrium conductivity, for different values of illumination.

The curves in Fig. 2 show the manner in which the conductivity should vary with the time for a given intensity of illumination when there are different amounts of the three components. This is again on the assumption that the reverse changes are small. All the forms of curves obtained with the different varieties of selenium are included in these curves. Also there is agreement in the fact that the highest sensibility selenium is that of the highest resistance and that of the negative variety is that of the lowest resistance. There are no disagreements between experiment and theory so far as these curves are concerned, unless we introduce a fact to be explained in a later paper, *i. e.*, that the conductivity of the *C* kind is small in comparison with that of the *B* kind.

Knowing the nature of the disagreement between experiment and theory when the reverse changes were supposed to be small, one can see at a glance that the particular disagreements should be removed if the reverse changes were not neglected. By taking into account the reverse changes as explained in the theory we not only removed the above discrepancies and obtained the curves showing all the characteristics required by the experimental results, but we also had a method of explaining the initial amounts of the three components and for explaining the recovery of selenium. Just what the agreement between the sign and the magnitude of the ratio of the sensibility to the initial conductivity may be cannot be defined further than is shown in Tables I. and II. There is no evidence of disagreement on this point. Satisfactory proof is lacking however in that Table I. does not consider all the possible relations. Theory and experiment agree on the following with regard to selenium of the variety found in the high sensibility of Giltay cells; the maximum conductivity occurs quicker with intense illumination than with faint; the maximum increases in value as the intensity increases; the equilibrium value of the conductivity increases with the intensity; for faint illumination the change of conductivity is almost proportional to the period of exposure.

There are some instances where no relation can be traced between theory and experiment. The ordinary effect of a rise of temperature is to produce a change in the conductivity in the same direction as that by light. But in the high sensibility cell the change by temperature is opposite to that by light. But since the temperature effect is in the same direction as in the pure metals and of about the same magnitude, we may say that the temperature effect is metallic in nature and refuse to explain it further. It is well known that the temperature effect in selenium cells is extremely large ordinarily. The curves in Fig. 6 illustrate this. It may be that the negative temperature effect exists in all selenium cells and that it is sometimes concealed by the much larger reaction temperature effect in the opposite direction. However the greatest difficulty in this line is with the light-negative variety of selenium. The change by heat is opposite to that by light and also to that in metals by heat. I have no explanation to offer further than to say that the indication is that the light and temperature produce entirely different effects in this variety of selenium, and the same effect in light-positive selenium.[1]

It is a noteworthy fact that in the Giltay cell a large potential difference produces a rapid increase in the conductivity which is followed by a decrease, almost identical to the changes produced by light except that the effects are not so large. As the two changes by light in the Giltay cells were found to be independent of the magnitude of the current one would naturally suppose that the large potential difference affects the conductivity as a result of electrical stresses in the selenium rather than as a result of the electric current. On this view the electrical forces would function in the dynamic equilibrium of the selenium.

Our experiments with selenium under pressure and those of Montén previously referred to show both a rapid and a slow change as noted for light and for high potentials. But the two changes here are difficult to measure accurately because of the simultaneous action of temperature. The equilibrium of selenium under pressure and temperature should be studied more carefully.

This dynamic equilibrium theory, if it satisfactorily explains all the observed phenomena, will still leave the whole subject in an unsatisfactory condition from one point of view. It will still remain to be explained why different varieties should have different rates of change. It may turn out that these different initial rates of change may arise from impurities which act as catalytic agents, or it may be if peculiar initial arrangements of the components are once established in the process of making, that there is an accompanying pressure or potential effect which maintains that peculiar arrangement. Some varieties of selenium do not have a fixed permanent stable equilibrium condition at once. They tend very slowly toward a new condition. In some cases moisture has been known to be the cause of such change but in others there is reasonable doubt. A semi-stable condition seems to exist in the light-negative selenium.

The way that light-sensitive selenium recovers when it is disturbed from its equilibrium condition by any agency is perhaps the strongest evidence in favor of the proposed dynamical theory. With the exception of some light-negative varieties of selenium, the selenium always recovers the conductivity that it possessed in the dark before illumination, and further the two changes that appear during the direct action also appear in the reverse process. The conductivity time curves may be called the reciprocals of the same curves for the action of light.

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[1] On the similarity of the light and temperature effects, see paper by Miss L. S. MacDowell, PHYS. REV., 31, p. 524, 1910.

If the view is accepted that the conductivity changes only when the amount of the conducting variety is changed, then there is obviously no discrepancy in Ohm's law.

Conclusions.

1. That light produces two changes in the conductivity of opposite sign in all light-sensitive selenium.
2. That the amount of the change is a function of the time of illumination as well as the intensity and character of the illumination.
3. That the selenium in the Giltay cell shows the same two changes under the action of high potential differences that it shows under the action of light.
4. That the character of the conductivity curves for the four known varieties of light-sensitive selenium can be explained by assuming the existence of three components in dynamic equilibrium, under given illumination, temperature, pressure and electrical potential differences.
5. That the effect of any agency that affects the conductivity of selenium is of the nature that it alters the rates of interchange between the components.
6. That the experimental results can be explained to a first order approximation on the assumption that only the B kind is conducting, of the three components which are in equilibrium according to the reaction $A \rightleftarrows B \rightleftarrows C$.
7. That if we accept the view here proposed the failure of Ohm's law becomes only an apparent and not a real failure.

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ON THE DISSOLUTION OF A METAL IN A BINARY SOLUTION, ONE COMPONENT ACID.

By Arden Richard Johnson.

According to the law of mass action, as given by Guldberg and Waage, the velocity of a chemical reaction is proportional to the product of the concentrations, or masses, of the reacting substances. If we are dealing with the action of an acid solution upon a metal, then according to the above law either doubling the area of the surface of the metal in action, or doubling the strength of the acid acted on, will increase twofold the rate of the chemical action, or rate of evolution of hydrogen from the reacting system.

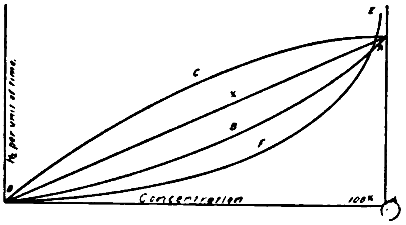

Fig. 1.

Fig. 1 illustrates diagramatically the meaning of the law when applied to the case of the action of metals on acids. Granted that we have in hand a metal and an acid solution between which there is possible a simple chemical reaction at any and all concentrations of the acid, then some point x on the diagram may represent the amount of hydrogen evolved for some particular concentration. Now according to the law of mass action, if the surface of the metal remains constant, a straight line drawn through x and the origin, O will represent the rate of chemical action at any and all concentrations.

Stated analytically the law, for the case in hand, takes one of the following forms:

$$dx/dt = K\,(a - x)\,S, \tag{A}$$

$$dx/dt = K. \tag{B}$$

Formula A is the more general one, in which a is the original amount of acid started with, S the surface of metal exposed, and k the proportionality factor. The second formula is derived from the first, if we assume the invariability of the acid concentration and area of surface exposed by the metal.

It is obvious that it is assumed in deriving the expressions above that the solvent used to vary the concentration of the acid must be an ideal one; *i. e.*, that the solvent must be absolutely nothing but a ***diluting medium*** for the acid.

However, to obtain such an ideal medium in practice is not an easy matter. *It is one of the objects of this work to discuss, in the light of experimentally obtained facts, those factors which cause the apparent divergence of theory and fact.*

For the sake of simplifying description and classifying subject matter I have divided into classes those factors, and agencies, which appear to me to have the greatest bearing on the dissolution of metals in acids.

(*A*) Physical or mechanical influences.	Products of reaction. Viscosity of solution.	Action of gas. Action of solids.
(*B*) Chemical influences.	(*a*) Interaction of solvent and solute. (*b*) Chemical effect of products of reaction.	
(*C*) Thermal influences.	Change of temperature during action.	
(*D*) Electrical influences.	Conductivity of solution. Local circuits due to impurities.	

Hardly a solution can be found upon which one or more of these sets of influences do not have a powerful action upon results obtained; and in some cases these effects almost cover up any evidence of the working of the law of mass action.

If we assume that we have no other detrimental forces working than the mechanical, we see that under all possible conditions that are apt to be met with, the actual chemical activity observed must be less than that demanded by the law of mass action, *i. e.*, on referring to the diagram, page 1, we should obtain a curve something like *A*, *B*, *O*. It is obvious that the products formed are a gas and a salt, and perhaps some sort of a film upon the surface of the metal. If the gas formed does not readily escape as soon as formed, or if the salt formed is not immediately soluble or disintegrable by the mechanical action of the hydrogen, the action must of necessity be lowered. Likewise, if there is a tendency toward the formation of a film of oxide, or other material, the action must be diminished.

But if we take into consideration the chemical influences (secondary chemical action) which might be exerted by the products of the reaction, it would not necessarily follow that the action in the above mentioned cases would be decreased; for the solubility of the gas, or salt formed, in the acid solution might accelerate the action to a considerable degree. It is a well-established fact that the addition of a bit of some foreign salt, soluble in the solution, can considerably enhance, or retard, chemical action. Perhaps some chemists would prefer to call the influence of the small quantity of salt "catalytic" in character. The curve expressing the relationship between chemical action and concentration might therefore fall either below, or above, as *A*, *C*, *O*, or, if we were particularly fortunate in the selection of our system, the curve might be a straight line.

There is, however, another concomitant in addition to the two just mentioned, which still farther complicates our problem, and that is the thermal effect accompanying the chemical action. We cannot have chemical action taking place without the simultaneous evolution or absorption of heat and a consequent change of temperature of the solution and metal.

The method used to eliminate as far as possible the effects of temperature will be dwelt upon more in detail later; suffice it here to say that such effects can be only approximately suppressed. In practically all of the cases under examination heat was evolved. While we do not know exactly the relations existing between rate of chemical action, quantity of heat evolved, and temperature produced, still it is quite safe to say that in most of the ordinary chemical reactions a rise of temperature causes a rise in the rate of the chemical action that is responsible for the evolution of the heat. Hence we may say that if the thermal accompaniments are considerable, all other conditions being ideal, the curve will fall above *A*, *X*, *O*, as *E*, *F*, *O*, and be more or less logarithmic in character.

While it is a fact that we understand a little, in a qualitative way at least, the effects of the above-mentioned influences and concomitants upon the working of the law of mass action, when applied to the action of metals upon an acid solution, yet in addition to these factors there is still another of very considerable importance in its bearing upon chemical activity, whose relation to the latter is not definitely understood. Nevertheless it is asserted by some that "*electrical conductivity*" is a "sine qua non" for chemical activity. *It is this alleged relationship between chemical activity and electrical conductivity which forms the main issue in this dissertation.* But to study this relationship itself, and to be able to draw trustworthy conclusions, requires a close study of the related influences and agencies already discussed.

To summarize as to the positive or negative effects of the principal influences upon the working of the law of mass action, as applied to solutions, I submit the following table: The symbol (−) means a depressing action upon the rate of chemical action; (+) an enhancing influence, and (o) no effect.

Influences.	Effects.
Mechanical.	−
Chemical (or catalytic).	+, or −, or 0.
Thermal.	+
Conductivity.	+, or −, (?) Is it necessary for *chemical action?*

Description of Apparatus.

Diagrams of apparatus used in carrying out the measurements of chemical activity are shown in Figs. 2–4. Fig. 2 shows the principal elements of the chief apparatus used. In the wooden rack (*A*) are arranged 11 graduated class eudiometer tubes in an upright position, closed end up. Each one of the eudiometer tubes dips into a glass beaker of 250 c.c. capacity, partly filled with water, oil, or mercury, as the case called for. *B* is a test-tube of 15 c.c. capacity which is so bent that it can extend into the beaker and empty under the eudiometer tube. Each test-tube is provided with a rubber stopper. The whole apparatus is modeled after the Victor Meyer gas density apparatus. All test-tubes rest in the trough (*C*) which may be filled with H_2O for keeping down the temperature of the reacting solution and metal.

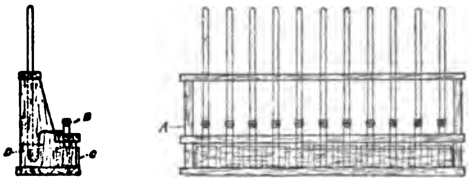

Fig. 2.

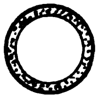

Fig. 3.

In using the apparatus each test-tube and its corresponding eudiometer tube was numbered from 1 to 11, from right to left, to prevent confusion and errors. Beginning with No. 1, which held 10 c.c. of 100 per cent. acid (or saturated solution), each succeeding test-tube to the left held 10 c.c. varying in strength from 90 per cent., by decrements of 10 per cent. to 0 per cent. acid or 100 per cent. solvent. The metal to be acted upon was cut from a rod of uniform diameter into small sections about 5 mm. long and 8 or 9 mm. in diameter. Both ends of the blocks were faced off smooth and then a rubber band stretched around the block as shown in Fig. 3, so that only the ends were exposed to the action of the acid. A block of metal thus prepared was placed in a certain test-tube containing the acid solution, the rubber stopper inserted, and after the first bubble of gas made its appearance at *D* the end of the tube was placed under the eudiometer and the gas collected for a known time consistent with accurate reading.

It is obvious that in cases where there is a tendency for a coating to form over the metal, or a layer of less concentrated solution in the case of slow action, some sort of shaking or stirring arrangement must be employed. Hence the apparatus shown in Fig. 4 was designed and used in a few instances. It consists simply of a row of test-tubes inverted over small beakers and all fastened in a common holder so arranged as to allow of slight lateral motion controlled by the eccentric arm and motor (*A*). The mouths of the test-tubes were placed as close as permissible to the bottoms of the beakers. Each beaker with its filled test-tube contained the same volume of solution. The cylinder of metal to be acted on was first mounted in a piece of rubber tubing as shown (*B*) and then slipped under the mouth of the test-tube, and in this position received sufficient knocking about to keep the surface free from the objectionable features stated above.

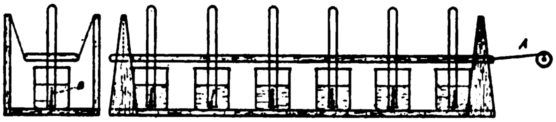

Fig. 4.

In order to study what relation the conductivity of a solution bears to the rate of dissolution of metals in the same, we must eliminate as far as possible the effects of those factors mentioned under heads *A*, *B*, *C*, page (—), as well as change of concentration of acid in solution during time of action, change of surface of metal exposed and decreased ability of solution for dissolving the salt formed. Practically the only way to do this is to *make the time for observing the rate of chemical action as short as is consistent with a reasonably accurate reading of the volume of gas evolved.*

MEASUREMENT OF CONDUCTIVITY.

All conductivity measurements of solutions were carried out by means of the regular Kohlrausch method. Care was exercised in all cases to thoroughly clean and dry the electrodes and cell with absolute alcohol and absolute ether, and dry in a current of air before each measurement. In practically all cases the measurements were made immediately before (and after) the measurements of the rate of chemical action, thus avoiding as much as possible changes in the conductivity of the solutions that might occur on standing.

ACID SOLUTIONS.

The acid used in most of the following experiments was glacial acetic, for the reason that it is not only a non-conductor when pure and attacks several metals, especially magnesium, with considerable avidity, but also because it is consolute at ordinary room temperature with a great number of both inorganic and organic solvents. Besides, most of the acetates are somewhat soluble in both inorganic and organic solvents, particularly magnesium acetate.

Discussion of Curves.

The first curves we shall inspect are those representing the rate of chemical attack of magnesium by acetic acid dissolved in water, and the corresponding conductivity curves. The upper curve, Fig. 5, shows a maximum chemical activity at about 45 per cent. acid. It will be noticed that the action is comparatively slow until a dilution of about 85 per cent. acid is reached, when the activity becomes quite considerable. Still it must also be noted that even for the pure acid the action is quite rapid.

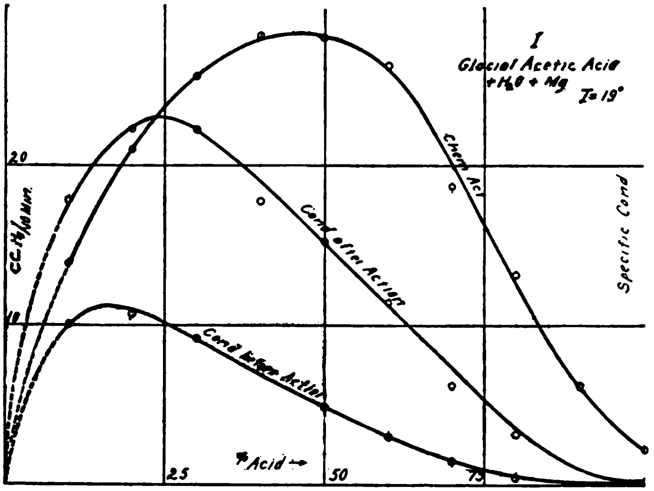

Fig. 5.

The conductivity curves in Fig. 5 are seen to be very similar in character. However, these points are to be noted: The maximum of the conductivity curve (taken before chemical action) does not fall at the same concentration of acid as does that of the chemical activity curve; nor do the maxima of the two conductivity curves (before and after action) coincide. This latter fact points out how the addition of the products of chemical action effect the conductivity—indeed, we should naturally expect them to. Also, the great similarity of the conductivity and chemical activity curves in form would surely cause one to suspect some intimate relationship between the two phenomena.

We shall now examine some curves obtained with a solution of tartaric acid in HOH. A saturated solution was made up and continually diluted by decrements of 10 per cent. from the original strength. Fig. 6 shows a definite maximum in the chemical activity curve corresponding exactly with that of the conductivity curve obtained after action. But the conductivity curve taken before action is different in that the maximum is not peaked, but rather flat.

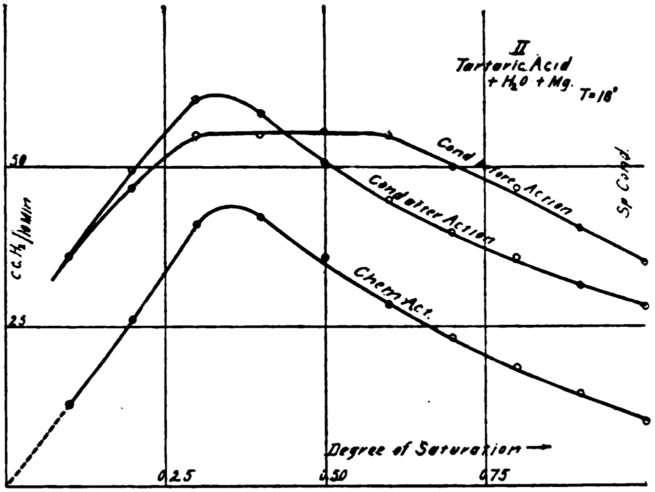

Fig. 6.

The curves in Fig. 7, obtained with the same acid, except that each solution was diluted to 33.3 per cent. absolute alcohol, show how differently the character of the conductivity curve may become through the addition of a foreign substance, yet the chemical activity curve remains quite unchanged.

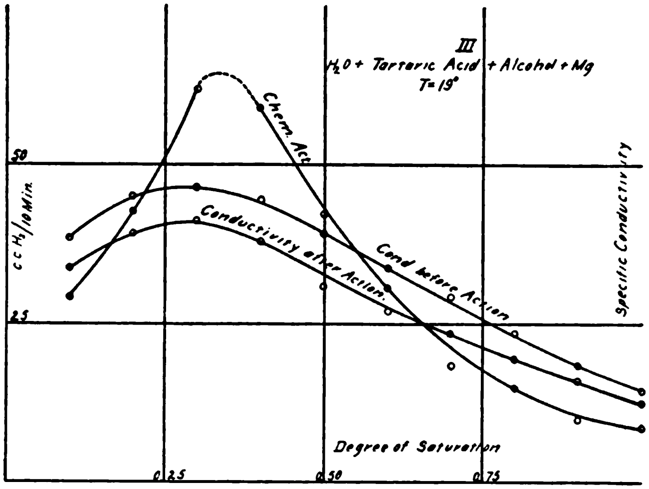

Fig. 7.

Of considerable interest are the curves obtained for oxalic acid dissolved in water forming ten sets of solutions varying from 10 per cent. of saturated to completely saturated solution at room temperature. The chemical action of this acid upon magnesium was very vigorous and a precipitate formed at all concentrations down to 30 per cent. of a saturated solution. But no crust formed on account of the great mechanical action of the hydrogen. It will be noted that these curves differ quite markedly from the preceding in that no maximum appears, and the chemical activity bears practically a linear relation to the acid concentration. So too is the conductivity curve quite parallel to the above curve.

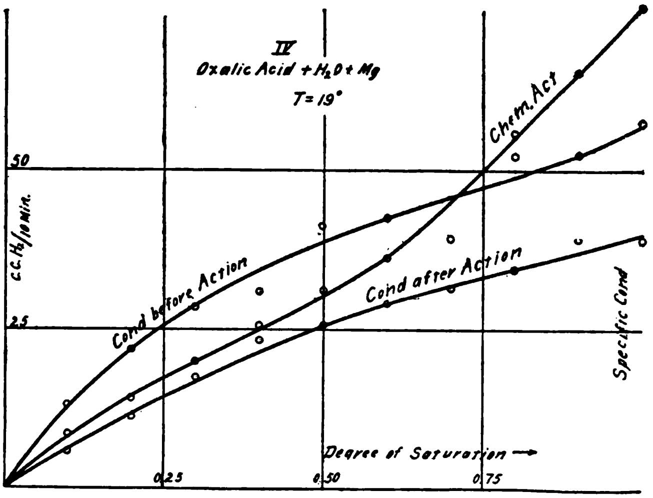

Fig. 8.

In comparing the last set of curves with those of acetic and tartaric acids, we are reminded that in the case of oxalic acid the influence of that force expressed by the law of mass action has been able to preponderate among the various factors effecting reactions and make itself evident. But why was its action so little in evidence in the two former cases? Here we should hardly guess that such a force was at work. If we turn back to the table of the various factors bearing upon the dissolution of metals in acids we shall see that neither the mechanical, electrical or thermal factors, under the conditions of the experiment, should interfere so powerfully with the working of the law of mass action. The solubility of the salts in all solutions is very great, the conductivities good and the thermal effect considerable. But as to the chemical influences alone! I think we are forced to agree with Dr. Kahlenberg's view of the chemical nature of solutions. As we gradually dilute acid with water, each step of the process gives us a substance which acts as a definite chemical compound in entirety, and exerts a specific chemical affinity for the metal in hand. Hence we should expect such a function—changing of chemical properties with dilution—to disguise very materially the effects of the law of mass action.

But it may properly be asked here how the conductivity changes are so parallel to the peculiarly changing functions of concentration already noted. This matter will be discussed in detail later on.

We shall now pass from a consideration of the above data, which have been obtained with water as solvent, to those cases in which certain organic solvents were used.

Absolute alcohol, the "water" of organic chemistry, we see on examining the curves of Fig. 9, gave conductivity curves, when using acetic acid, very similar in appearance to those obtained with water as solvent, but the chemical activity curve was almost a straight line, indicating that the effect of concentration is independent of the other factors. In this case we have changed the order of the magnitude of the conductivities of the various solutions in alcohol very much from what they were in the case of water, and while the chemical action shows up as a different sort of function yet the character of the curve expressing change of conductivity remains much the same. We might, however, explain this latter fact by assuming that the alcohol and acid interact, yielding H_2O as one of the products and this, acting on the acid, causes the similar electrical conductivity curve.

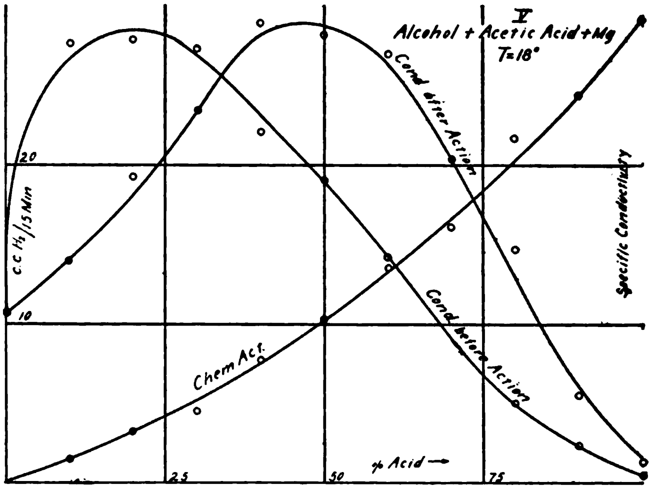

Fig. 9.

In ethyl-acetate as a solvent we have a strange state of affairs, in that, although the magnitude of the conductivity of the solutions is very small, still the curve representing the conductivity is very similar in character to the chemical activity curve and would cause one to suspect an intimate relationship between the two.

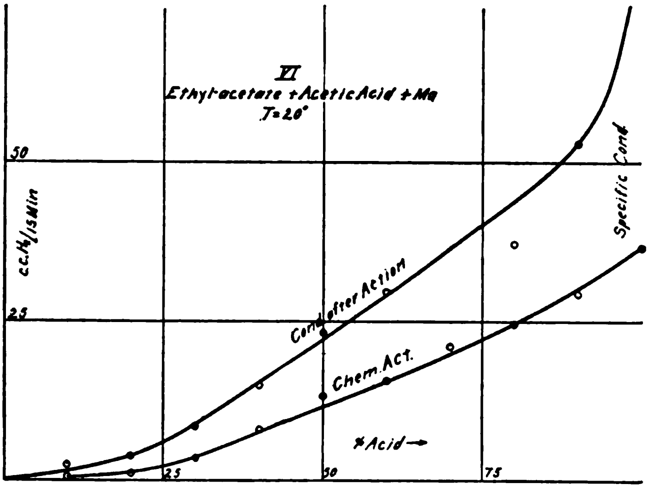

Fig. 10.

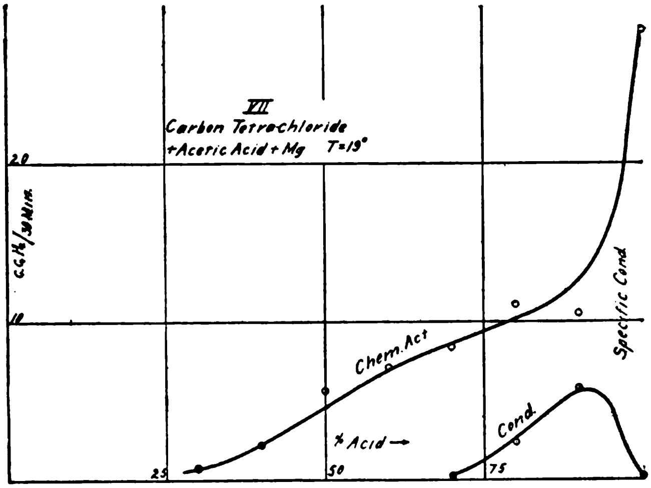

Fig. 11.

Carbon tetrachloride and also acetic anhydride used as solvents, both yield very poorly conducting solutions, yet the chemical activity curves were obtained very easily. The rapidity of action in the case of the acetic anhydride was quite considerable as the curve will show. However, in neither case is the conductivity anything like the reaction curve. In the case of the conductivity curve for CCl_4 a maximum was observed.

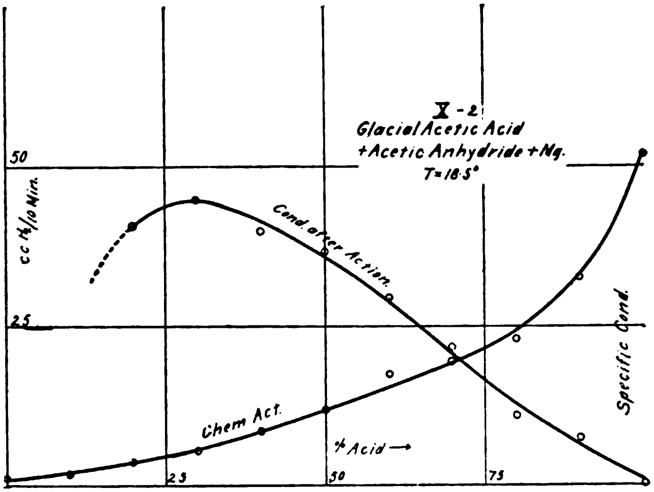

Fig. 12.

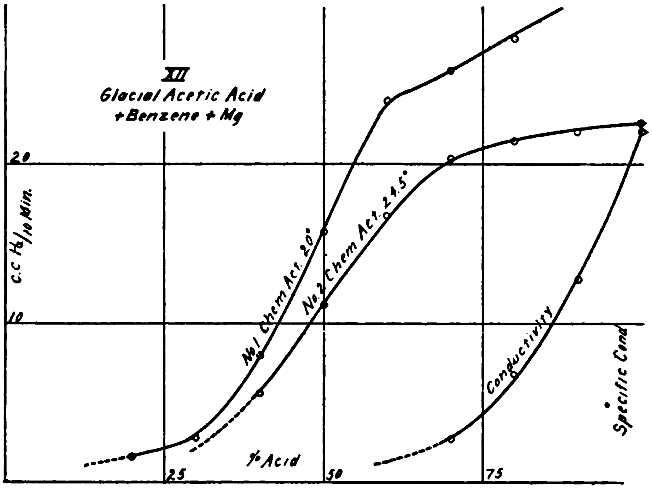

Fig. 13.

Such an event might be due to the presence of a trace of water dissolved in the solution. The validity of this argument will be treated of later. The chemical reaction curve for acetic anhydride is quite remarkable in that it is almost a straight line over most of its course.

A curve plate was obtained when using carbon di-sulphide as solvent for the glacial acetic acid. Some trouble was experienced in that the two substances were not soluble in all proportions at the temperature of the room. The solutions obtained were of very low conductivity, and a

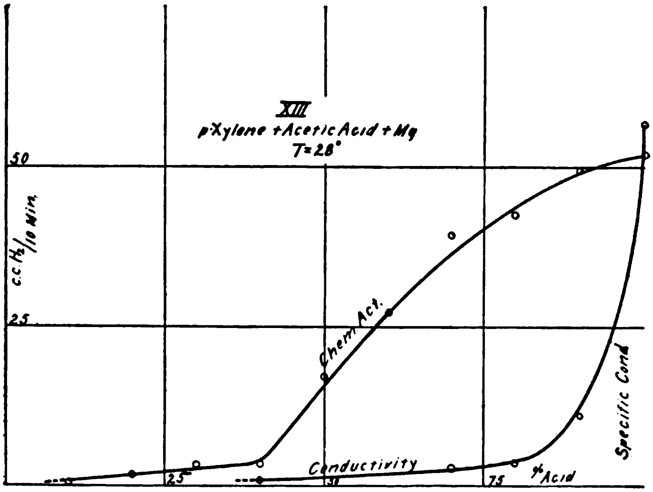

Fig. 14.

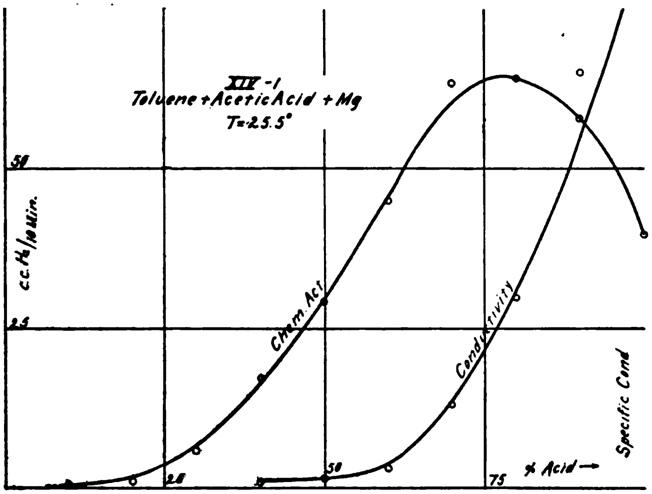

Fig. 15.

small addition of the CS_2 to the acid caused a very great depression of the rate of chemical action as shown by the curve. But the depression is really unduly great, partly because of the formation upon the magnesium of a rubber-like coating during the reaction.

We cannot maintain that the depression of the action in CS_2 solution of acetic acid upon magnesium is due principally to the great depression of the conductivity in the face of the mechanical action of the products of the reaction. And this fact is farther borne out in the case of a solution

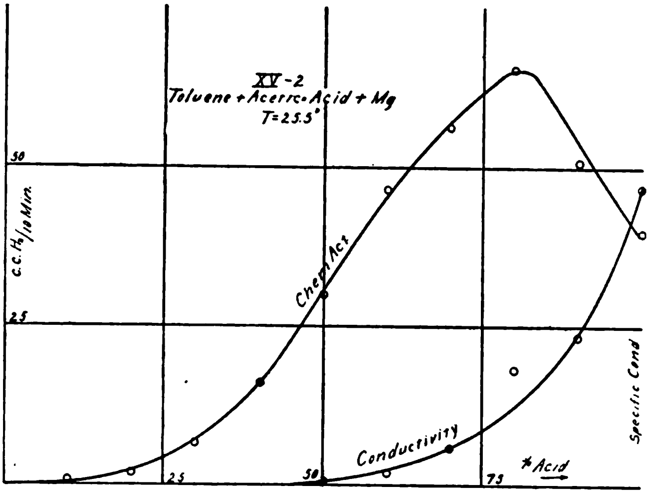

Fig. 16.

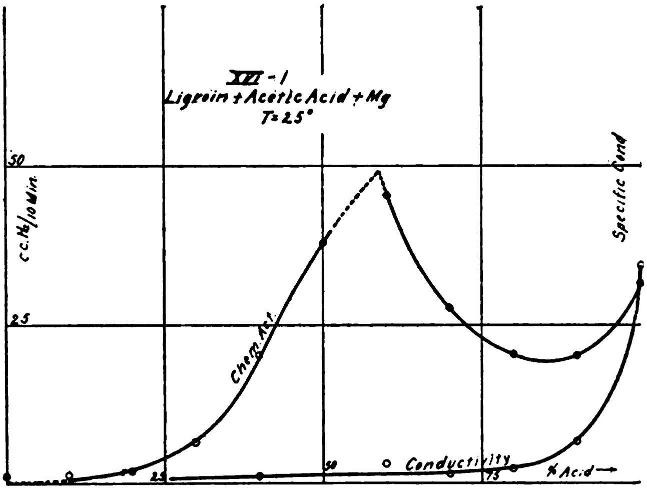

Fig. 17.

of acetic acid in di-ethyl ether, for here the fairly rapid chemical action persists to at least 75 per cent. acid concentration in spite of a tendency toward the formation of a sticky coating on the magnesium.

Benzene as solvent shows almost unabated action down to 60 per cent. acid. No film or precipitate could be noted at all so long as the solutions remained at about 18°, but on raising the temperature a black coloration appeared which turned white on exposure to air.

Similar to the preceding is the working of p-xylene as solvent. This

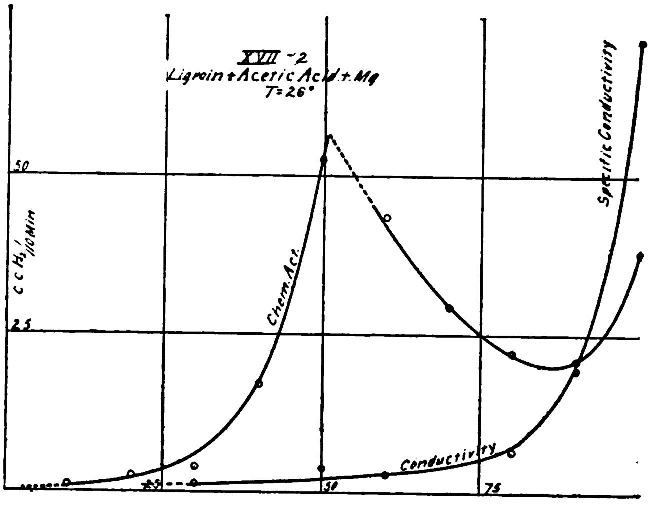

Fig. 18.

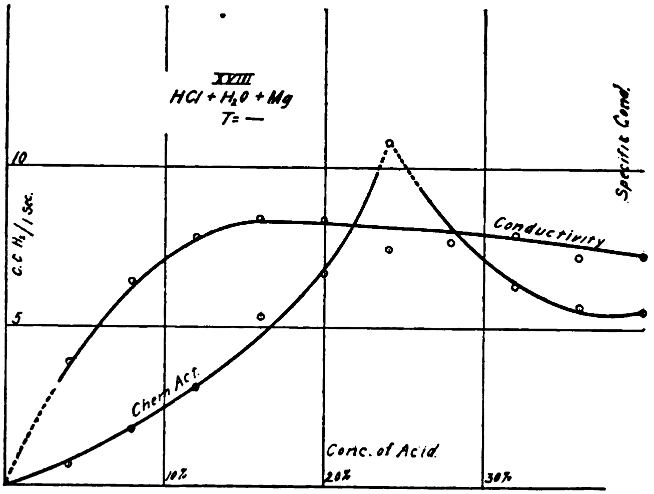

Fig. 19.

set of curves was obtained on a hot summer day and the black color appeared on the metal; still the action decreases only slowly to 60 per cent. acid.

After watching the course of results using these aromatic hydrocarbons as solvents it occurred to me that no trouble would be experienced at all in getting entirely similar results using other hydrocarbons of the series and also aliphatic hydrocarbons. So toluene was next tried. But to my surprise the character of the chemical activity curve was quite different, in that instead of a depression of the reaction on addition of toluene an actual increase of action was noted. That is, a definite maximum was noted in the curve. This result was so surprising that a second entirely different sample was obtained and purified. But curve No. 2, Fig. —, testifies to similar results. The two curves are not absolutely alike, but are of a similar nature. Now this curve showing a maximum obtained when using an organic, non-conducting solvent for non-conducting glacial acetic acid is very interesting because it brings back to our minds a remembrance of parallel cases when acids are dissolved in inorganic, good conducting substances.

A still more striking curve is that obtained for the action of acetic acid, dissolved in ligroin, upon magnesium. This curve exhibits cusped portions and a maximum point, at first a considerable depression of the action, and then a rapid rise to a rate greater than for the pure acid, then a swift fall again. The figures for rate of chemical action are seen to be of no mean values, yet the results for electrical conductivity would appear to be rather discouraging to rapid chemical action in the light of prevailing theories.

Comparison of Chemical and Conductivity Data.

According to the prevailing electrochemical or ionization theory, we should rightly expect in most of these cases where factors A, B and C were favorable or neutral to chemical action, that the chemical activity and conductivity curves would be somewhat similar; and that for acid solutions of the same concentrations in different solvents, but of equal conductivity, we should expect rates of chemical action of the same order of magnitude. Yet an examination of the curves and data herein given will reveal no such regular relation. Solutions having extremely low conducting power are in many cases acted upon by the magnesium almost half as fast as in the comparatively good conducting aqueous solutions.

In order to facilitate a comparison of data for different solvents, Table I. has been arranged. After columns containing the names of solvents, temperatures and dielectric constants, are columns 1, 2, and 3, giving the average rate of chemical action, and average conductivity for all concentrations of acetic acid in a particular solvent. To obtain these average values the ordinates of the curves were added up and then the sum divided by their number.

It is worthy of notice that aqueous solutions of tartaric and oxalic acids, while yielding fairly good conducting solutions, are not attacked any more readily by magnesium than are several other solutions of acetic acid in hydrocarbons. Even if we center our attention upon a single solvent we see that the magnitude of the conductivity can be varied within wide limits without appreciably effecting the rate of hydrogen evolution, all other conditions remaining practically the same. For example, compare the different values given for toluene, ligroin, and acetic anhydride.

TABLE I.

Solvent for Acetic Acid.	Temp.	Dielectric Constant of Solvent.	App. Av. Specific Conductance.	Av. H_2 Evolution per 10 min.
Water	19°	81.12	4545(-6)	86.95
Alcohol	18°	26.80	18(-6)	8.38
Ethyl acetate	20°	5.80	14(-6)	9.70
Ether	21°	4.36	——	7.04
Acetic anhydride	27°		8.5(-6)	34.78
Carbon tetrachloride	19°	2.25	8.0(-6)	1.97
Carbon bisulphide	18°	2.63	——	1.77
Benzene no. 1	20°	2.29	45.(-6)	16.17
Benzene no. 2	24.5°	2.29	45.(-6)	23.12
Toluene no. 1	25.5°	2.31	9.(-6)	31.31
Toluene no. 2	25.5°	2.31	5.(-6)	29.20
Ligroin no. 1	24°	1.85	2.(-6)	20.61
Ligroin no. 2	26°	1.85	6.(-6)	22.16
Xylene	28°		5 (-6)	22.56
H_2O as solvent of:				
Oxalic acid	19°	——	0.181	35.49
Tartaric acid	18°	——	0.03+	32.00
Tartaric acid plus alcohol	19°	——	0.016	11.90
Hydrochloric acid	——	——	1.735	2930.92

Be the above facts as they may, it appears as though we might center our attention upon the chemical activity curve and regard it as the *resultant* of all other curves expressing relationships between concentration of acid in solvent and all other forces, as: mechanical, thermal, electrical and others.

It is only proper that I close this dissertation by acknowledging my indebtedness to Dr. L. Kahlenberg, of the University of Wisconsin, for many suggestions in this work.

THE POSITIVE POTENTIAL OF ALUMINUM AS A FUNCTION OF THE WAVE-LENGTH OF THE INCIDENT LIGHT.

By J. R. Wright.

LENARD[1] was the first to investigate the velocity with which electrons are emitted from a metal plate in a vacuum when illuminated by ultra-violet light. He found that the velocities of emission were independent of the intensity of the incident light, but varied for different metals. He, therefore, concluded that the effect was a resonance phenomenon, the velocity with which the electrons were emitted being derived from the energy of the electron within the atom, the light playing simply a releasing role. More recently Ladenburg[2] investigated the relation between the initial velocities of emission and the wave-length of the incident light. He found that for a given metal the maximum initial velocities were directly proportional to the frequency of the incident light. Tests were made on the three metals, platinum, zinc and copper. Ladenburg and Markau,[3] by obtaining the velocity distribution curves, have shown that for a given region of the spectrum the electrons emitted have velocities lying within narrow limits. They, therefore, conclude that the photo-electric effect is purely a resonance phenomenon; the emission of the electrons will occur only when the frequency of the light bears a definite relation to that of the electron within the atom, and consequently for any given wave-length the velocities of emission ought to be all equal or closely grouped about a mean. The range of wave-lengths used by Ladenburg and by Ladenburg and Markau was from $\lambda 2700$ to $\lambda 2000$. Hull,[4] working in the region of very short wave-lengths, the so-called Schumann rays, found that the velocities of emission of electrons from a plate covered with lampblack increased with the frequency of the light, and concluded that, within the limit of accuracy with which this region of the spectrum is known, the proportionality discovered by Ladenburg holds for these very short wave-lengths. Three regions of the spectrum were obtained by means of absorption screens.

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[1] P. Lenard, Ann. d. Phys. II., p. 259, 1900; VIII., p. 149, 1900.

[2] E. Ladenburg, Phys. Zeitschr., VIII., p. 590, 1907.

[3] Ladenburg and Markau, Phys. Zeitschr., IX., p. 251, 1909.

[4] A. W. Hull, Am. Jour. of Sc., XXVIII., p. 251, 1909.

The shortest wave-lengths of the three regions were approximately λ1710, λ1450 and λ1230. His conclusions are based on the assumption that the maximum velocities are due to the shortest wave-length in each region.

If the electrons, emitted under the influence of the light, are constituent parts of the atom, which owe their escape to resonance, then the velocities of emission can be determined by measuring the maximum positive charge acquired by a metal when illuminated in a perfect vacuum; for if m is the mass and e the charge of the electron, v the velocity of emission, and V the positive potential just sufficient to pull back the fastest electrons to the plate, then evidently

$$\tfrac{1}{2}mv^2 = eV \quad \text{or} \quad v = \sqrt{2Ve/m}.$$

The values of the positive potentials obtained by the earlier observers have ranged from 0 to 5 volts for different metals. Millikan and Winchester,[1] made determinations on eleven metals, obtaining values which varied from 0 for lead to 1.336 volts for silver. More recently Millikan,[2] working on the same metals and under identical conditions, found that by prolonged illumination with very intense ultra-violet light the positive potentials were increased from ten to thirty times the values previously obtained.

The importance of these results made it highly desirable that the relation between these new positive potentials and the wave-length of the incident light be determined. The investigation, the results of which are given in this paper, was undertaken with this object in view.

Two general methods were available for determining the velocities of emission; either an insulated plate, with earthed surroundings, is connected to an electrometer and the maximum positive potential, acquired by the plate when illuminated by ultra-violet light, measured, or the photo-electric current, which flows from the illuminated plate to an oppositely placed receiving plate, is observed, when a potential difference exists between the plates. The first method was adopted as more direct and better adapted to the object of the investigation.

The form of tube adopted and the arrangement of apparatus is shown in Fig. 1. The light from the spark passed through the spectrometer, fitted with the quartz lenses, L_1 and L_2, and the quartz prism, P, through the quartz window, Q, and fell upon the insulated aluminum plate, A, of 3 cm. diameter, which was connected to one pair of quadrants of a well-insulated Dolezalek electrometer, E. The electrometer gave a deflection of about 4 cm. per volt for a scale distance of 125 cm. G is a brass tube, blackened on the inside, and fitted with the two washers, w_1 and w_2, so arranged that practically no light fell upon the inside of the tube. *G* was kept earthed throughout the experiment, and was metallically connected to the gauze wire, *g*, which completely surrounded *A*. The two slits, s_1 and s_2, of the spectrometer were 1 mm. in width. In order to screen from electrostatic effects, the tube was entirely surrounded by the earthed metal case, *M*. The potentiometer arrangement, consisting of the two resistances, R_1 and R_2, and the batteries, *B*, was used to place a positive charge on *A*.

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[1] R. A. Millikan and Geo. Winchester, Phil. Mag., 6, p. 188, 1907.

[2] R. A. Millikan, PHYS. REV., XXX., 2, p. 287, 1910.

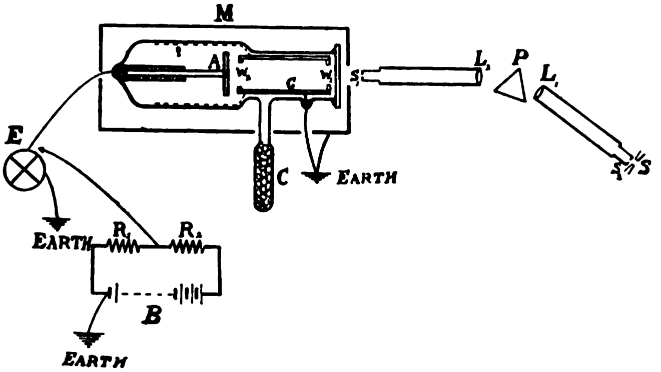

Fig. 1.

The source of ultra-violet light was a very powerful spark between metallic electrodes, the spark gap being about 2.5 mm. in length. The spark electrodes, with eight large Leyden jars in parallel, were made the terminals of the secondary of a large Scheidel transformer, the primary carrying 10 amperes at a P.D. of about 25 volts. Of several metals tested as electrodes zinc, cadmium, and iron were found to be the most efficient.

The vacuum was the best that could be obtained by the Dewar method. The tube was attached to a mercury pump, the bulb, *C* (Fig. 1) containing cocoanut charcoal being heated to 360° C. during the process of exhaustion. A glow discharge was passed from *A* to *G* for several hours in order to denude the electrode, *A*, as far as possible of occluded gases. The exhaustion was continued until a vacuum of approximately 0.00001 mm. mercury, as given by a McLeod gauge, was obtained. The tube after a period of six months, during which time the vacuum remained constant, was then sealed off from the pump and set up as shown in Fig. 1.

The method of observation finally adopted was to place on *A*, by means of the potentiometer arrangement, a positive charge and then illuminate with the ultra-violet light until the electrometer gave the natural leak of the system, which was about 0.8 mm. per minute. This point was then observed and the positive potential necessary to give the same deflection measured. By this method of observation the period of illumination was greatly diminished, thereby preventing excessive heating of the spark terminals. This method was checked by comparison with that of direct observation, that is, by starting with A at zero potential and illuminating until the maximum positive potential was reached. The two methods were found to agree consistently.

During the preliminary observations the spectrometer was removed and the spark placed in the position occupied by s_1. The first observation on the positive potential with unresolved light gave a value of 0.25 volt. The plate was then illuminated by ten minute intervals for several hours a day during a period of three weeks. Frequent determinations of the positive potentials were made between illuminations. The positive potential was found to increase consistently with illumination until a value of 13.5 volts was reached, when further exposure to the light apparently produced no effect.

No claim is made that this value of 13.5 volts is the true maximum positive potential for aluminum. Without much doubt light reflected from the disk, A, will cause electrons to be emitted from the brass tube, G, which will flow to A under the influence of the electrical field. Moreover, as O. v. Baeyer[1] has shown, slow electrons will be very strongly reflected, which, as in the case of electrons produced by the reflected light, will tend to decrease the observed value of the positive potential. To what extent the positive potential will be influenced by these causes seems to be still an open question. Ladenburg and Markau (*l. c.*) found that prevention of reflection had an appreciable effect both on the value of the positive potential and the velocity-distribution curves, while Klages,[2] with a similar arrangement of apparatus, obtained results from which he arrived at exactly opposite conclusions. In the arrangement of apparatus used in the present investigation the only precaution taken to prevent reflection was the blackening of the inside of the tube, G. Since the chief object of this investigation was to determine the relation that exists between the positive potential and the wave-length of the incident light, a slight difference between the measured and the absolute value of the potential would hardly exert an appreciable influence on the results obtained. The problem of obtaining the absolute values of the positive potentials is being made the subject of a separate investigation in this laboratory.

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[1] O. v. Baeyer, Verh. d. D. Phys. Ges., 10, p. 96, and p. 953, 1908.

[2] A. Klages, Ann. der Physik, IV., 31, p. 343, 1910.

Before obtaining the relation between the positive potentials and the wave-length of the incident light a determination was made of the rate at which the positive potential was assumed for any narrow spectral region. Starting with *A* at zero potential the deflection of the electrometer corresponding to the positive potential was read every ten seconds. Light of the mean wave-length 2166 from the zinc spark was used. The results are shown graphically in Curve I., the abscissas corresponding to the time and the ordinates to the electrometer deflections. On account of the heating of the spark terminals it was impossible to continue the illumination until the maximum potential was reached. The maximum deflection represented in Curve I. corresponds to a positive potential of 12.3 volts. The smoothness of the curve shows plainly the degree of accuracy with which observations on the positive potentials could be obtained under the conditions which existed throughout the investigation. Since the conclusions to be drawn from the positive potential curves (see V., VI. and VII.) must depend largely on the accuracy of the observations it was thought essential to introduce a curve illustrating this point. No further importance, than the above mentioned, is to be attached to Curve I.

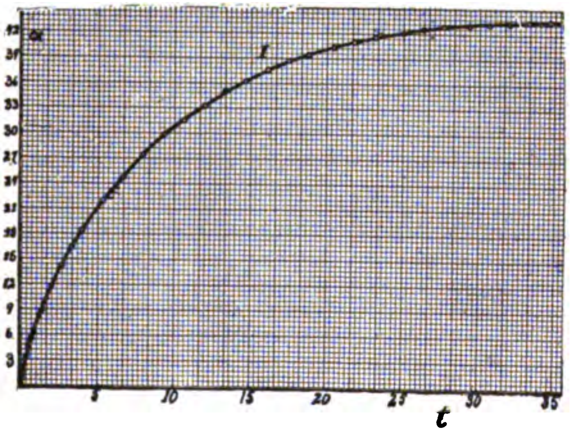

Fig. 2.

Tests were then made on the photo-electric sensitiveness of the disk, *A*, for light from different sources, the results for sparks between zinc, cadmium and iron being given in Curves II., III. and IV. respectively. The method of observation was that usually followed in such determinations. The disk was charged to a negative potential of ten volts, and then illuminated for one-minute intervals with light of different wave-lengths, and the corresponding electrometer deflections read. The wave-lengths are plotted along the axis of abscissas and the electrometer deflections, which are proportional to the photoelectric current, along the axis of ordinates. The intensity of the light was kept as nearly constant as possible during these observations. A study of these curves in their relation to the positive potential curves will be taken up later.

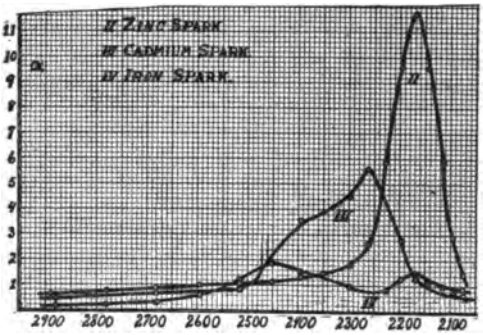

Fig. 3.

Determinations were then made on the positive potentials for definite wave-lengths in the region extending from λ2878 to λ2073. A typical series of results obtained in this manner, using light from the spark between zinc electrodes, is given in Table I., and represented graphically in Curve V. The ordinates of the curve represent the square roots of the positive potentials and the abscissas the wave-lengths. During the series of observations represented in Table I. the charcoal bulb was immersed in liquid air. Several sets of observations were taken without using liquid air, the only deviation from the above results being a lowering of the positive potentials by about 5 per cent. During any series of observations the intensity of the light was kept as nearly constant as possible, but no effort was made to keep the intensity the same for different sets of observations. On the contrary the length of the spark gap was purposely changed from time to time, and the current through the primary of the transformer was varied through values ranging from 8 to 15 amperes. The capacity in parallel with the spark was, however, kept constant during the entire course of the investigation. Photoelectric current curves were generally taken just preceding observations on the positive potentials.

A variation of the experiment was then made by using the light from the cadmium and iron sparks. The results are given in Tables II. and III., and represented graphically in Curves VI. and VII. A study of the Tables I., II., and III., and Curves V., VI., and VII. shows that contrary

TABLE I.

Zinc Spark.

δ	λ	V	$\sqrt{V}$
3° 48′	2,878	6.75	2.598
4° 48′	2,678	7.25	2.693
5° 48′	2,513	7.88	2.807
6° 48′	2,392	8.71	2.951
7° 48′	2,294	9.69	3.113
8° 18′	2,258	10.57	3.251
8° 48′	2,226	11.58	3.432
9° 18′	2,195	13.45	3.667
9° 48′	2,166	14.19*	3.767
10° 18′	2,139	13.77	3.711
10° 48′	2,113	12.99	3.604
11° 18′	2,092	11.96	3.458
11° 48′	2,073	11.19	3.345

δ = deviation (Na = 0).
V = positive potential.
λ = wave-length.
* = 14.19 volts = 2.23×10^8 cm./sec.

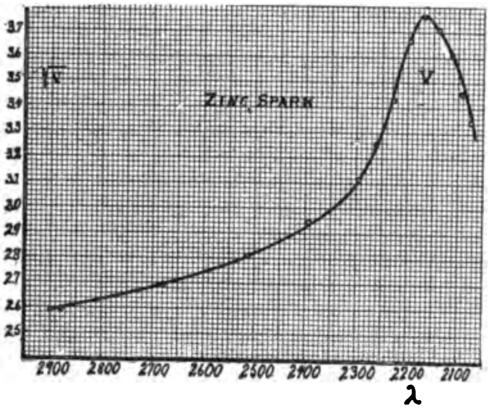

Fig. 4.

to the results found by Ladenburg and by Hull, the positive potential does not increase as a linear function of the frequency of the incident light, but reaches a maximum for λ2166. Using different sources of light is without influence either on the position of the maxima or on their numerical value. The slight difference in the numerical values of the maximum points may be ascribed to two causes: (1) observational errors, and (2) changes in the natural leak of the electrometer system, which varied slightly with weather conditions. The form of Curve VI. is slightly different from that of Curves V. and VII. This variation is probably due, at least to a considerable extent, to the effect of the reflected light. Since the relative intensities of the light from the different sources varied considerably with the wave-length, it is to be expected that the effect due to the reflected light will also vary, thereby causing a slight variation in the measured positive potentials. Part of the variation may, however, be due to the difficulty experienced in locating the points for wave-lengths ranging from λ2900 to λ2650. The readings around the maximum could easily be determined within 3 mm. in a total deflection of about 500 mm., while for the range from λ2900 to λ2650 the observational error was considerably greater, since for these wave-lengths the photo-electric sensitiveness was comparatively small, as is shown by Curves II., III., and IV.

Table II.

Cadmium Spark.

δ	λ	V	$\sqrt{V}$
3° 48′	2,878	7.80	2.794
4° 48′	2,678	8.27	2.875
5° 48′	2,512	9.14	3.001
6° 48′	2,392	10.46	3.234
7° 48′	2,294	12.10	3.478
8° 18′	2,258	12.92	3.592
8° 48′	2,226	13.37	3.652
9° 18′	2,195	13.77	3.706
9° 48′	2,166	14.04	3.742
10° 18′	2,139	13.66	3.698
10° 48′	2,113	13.22	3.636

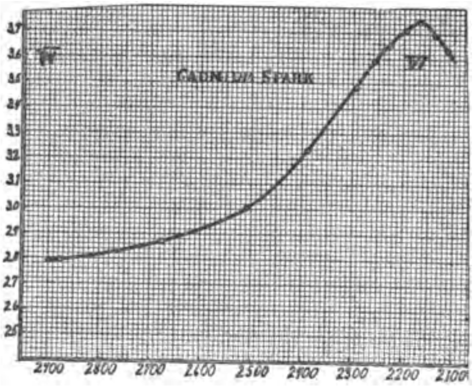

Fig. 5.

TABLE III.

Iron Spark.

δ	λ	V	$\sqrt{V}$
5° 48′	2,512	8.59	2.931
6° 18′	2,448	8.88	2.980
7° 18′	2,347	10.09	3.176
8° 18′	2,258	11.13	3.334
9° 18′	2,195	13.01	3.604
9° 48′	2,166	14.16	3.759
10° 18′	2,139	13.61	3.688
10° 48′	2,113	12.93	3.597

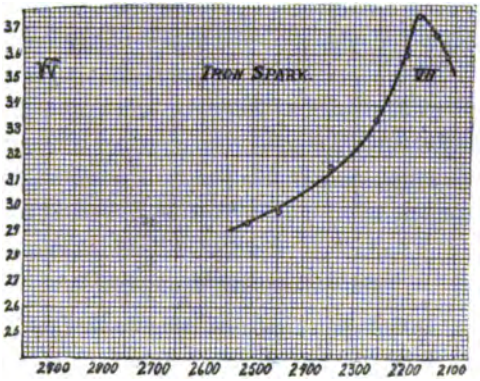

Fig. 6.

The complete independence of the positive potentials on the intensity of the light is evident from a comparison of Curves II., III., and IV. for the wave-length 2166 which gives the maximum potential for all three sparks. While the relative intensities of the light from the three sparks for this wave-length were approximately as 10 : 12 : 100 the widest variation of the positive potentials from the mean is less than 0.5 per cent. This is even more conclusively shown by other sets of observations in which the ratio of the intensities shows wider variation.

The lack of agreement between these results and those of Ladenburg and of Hull is probably due to some change that takes place on the surface of the metal during illumination. Whether this change is due to the breaking down of an electrical double layer of gas, or simply to a cleansing of the surface, or to a combination of causes, cannot be easily determined. That the emission of electrons from the metal under the influence of the light did actually cleanse the surface was without doubt the case in these experiments. The use of the disk as a cathode or a discharge from an induction coil, during the early stages of exhaustion of the tube, had slightly tarnished the surface of the metal. After the disk had been illuminated for some time it was found that the part illuminated was decidedly brightened, presenting the appearance of freshly polished aluminum, while the unilluminated portion around the edge remained dark. That the increase in the positive potential from 0.25 volt to 14.1 volts can be ascribed solely to a cleansing process seems very unlikely in the light of the results obtained by Millikan (*l. c.*) on metals which were polished without oil, and had not been used as a cathode for an induction-coil discharge.

Whether other metals will show a similar relation between the positive potentials and the wave-length of the incident light is an important question which is being investigated at the present time by Professor Millikan and the author.

Before concluding, the author desires to express his thanks to Professor Michelson and members of the Department of Physics for the interest manifested in the work, and especially to Professor Millikan, at whose suggestion this investigation was undertaken, for many valuable suggestions.

SUMMARY OF RESULTS.

The positive potential of aluminum was found to increase from 0.25 volt to 14.1 volts as the result of long exposure to very intense ultraviolet light. The relation between this comparatively high positive potential and the wave-length of the incident light has been determined, and it has been found that, contrary to the results obtained by Ladenburg and by Hull, the positive potential reaches a definite maximum for $\lambda 2166$. Using light from different sources is without effect either on the value or the position in the spectrum of the maximum point.

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A METHOD OF MEASURING THE FLUCTUATIONS IN A RAPIDLY VARYING RESISTANCE.

By F. C. Brown and W. H. Clark.

SOMETIMES it becomes necessary to measure a variable resistance which changes during short intervals of time. We have found that by placing the variable resistance in one arm of a Wheatstone's bridge circuit we can express its average value for any interval of time in terms of the throw of a ballistic galvanometer where the galvanometer is thrown into the circuit by means of a pendulum for the desired interval of time which must be small compared to the period of the galvanometer. How small this interval should be is also determined by the rapidity with which the resistance changes. If the time is made sufficiently short the average resistance practically becomes the actual resistance at the middle of the interval.

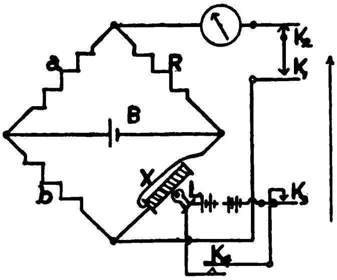

Fig. 1.

Theory.

The theory of the method is quite elementary. Consider resistances without appreciable capacity or self-induction to be connected in a Wheatstone's bridge circuit as shown in Fig. 1. Suppose the battery resistance to be small compared to the other resistances. Let the balance be disturbed by changing the resistance in the variable arm by a small amount Δx. Then it can easily be shown that the current through the galvanometer is

$$i = \frac{E(bk_2 + k_1aR)(\Delta x)}{(k_1x + k_2)^2}, \tag{1}$$

where a, b, R and x and G are the resistances in the circuit,

$$k_1 = Gb + aG + bR + ab + aR,$$

$$k_2 = aRG + bRG + abR,$$

and

E is the electromotive force of the battery.

The quantity of electricity that is sent through the galvanometer may be expressed as

$$\Delta Q = i\Delta t,$$

or

$$Kd = i\Delta t, \tag{2}$$

where K is the constant of the ballistic galvanometer as obtained by discharging a known quantity of electricity through it and where Δt is the length of time that the current flows through the galvanometer. By combining equations (1) and (2) we obtain for the change of resistance,

$$\Delta x = \frac{Kd(k_1x + k_2)^2}{\Delta t E(bk_2 + k_1aR)}. \tag{3}$$

Now if Δx is small compared with x we may set

$$\frac{K(k_1x + k_2)^2}{E(bk_2 + k_1aR)} = C,$$

a new constant for a given set of resistances, and a given battery and galvanometer, and then

$$\Delta x = \frac{Cd}{\Delta t}. \tag{4}$$

The meaning of this equation (4) is that the change of resistance in the variable arm of the bridge is directly proportional to the deflection of the ballistic galvanometer and to the constant C, and inversely proportional to the interval Δt during which the galvanometer is in circuit. The change of resistance then can be calculated provided that it is small compared to the value of the resistance necessary to balance the bridge circuit. It will be noted that we have supposed that there is no appreciable damping of the galvanometer while it is in closed circuit during the interval Δt. The validity of this assumption will be considered later in the paper. Also the self-induction of the galvanometer is regarded as having no influence on the magnitude of the deflection.

Application to the Measurement of Small Changes of Resistance.—In order to test the linear relations between the deflection and the change of resistance and between the deflection and the interval Δt, known resistances were placed in the Wheatstone's bridge circuit shown in Fig. 1. The pendulum and keys were similar to those described in Carhart and Patterson's Electrical Measurements. A ballistic D'Arsonval galvanometer made by Leeds and Northrop was used. It had a period of 22.4 sec. A ballistic galvanometer with a period of 48.8 sec. was also used. To find the variation of the deflection with the change of resistance, the keys k_1 and k_2 were placed a distance apart such that the interval during which the galvanometer was in circuit was $\Delta t = .05$ sec. Then the resistance in the variable arm was varied by different amounts previous to each reading. The readings were taken after the pendulum had operated the keys k_1 and k_2. In this test the resistance remained constant throughout the interval. All the observations that were taken are recorded in Curve III. of Fig. 2. It will be noted that there is only a small percentage error in any single observation and further that for a change of resistance as large as 800 ohms there is only a slight variation from the linear relation. For changes as large as $\Delta x = 200$ there is obviously complete agreement between the theory and experiment. It may be concluded here that the deflection is proportional to the change of resistance.

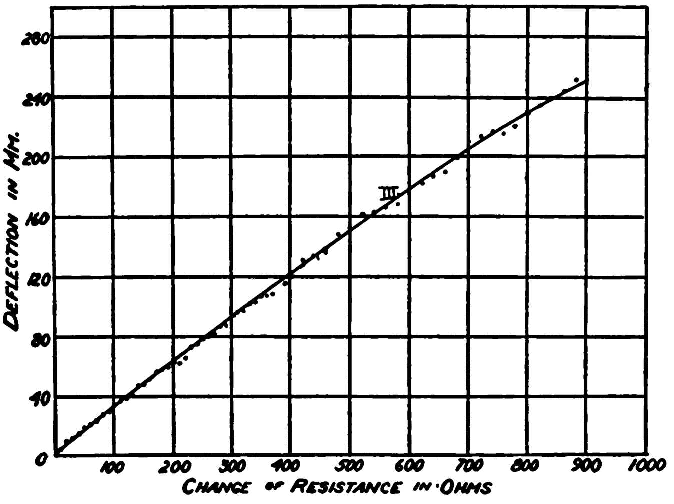

Fig. 2.

Relation between deflection and change of resistance; $a = 100$, $b = 100$, $R = 5000$, $x = 5000 - 4120$ ohms.

In order to test the relation between the deflection and the length of time that the galvanometer was in the circuit the variable resistance was changed a given amount, 15 ohms, from that required for equilibrium, and the distance between the keys k_1 and k_2 was varied. Observations were taken for both of the galvanometers referred to. These are shown in Curves I. and II., Fig. 3. Between .01 and about .12 sec. the linear relation required by equation (4) holds but from 0.12 sec. to 0.4 sec. there is a slight tendency for the deflection to grow less as the interval is increased. This slight downward bending of the time-deflection curves for larger intervals of time probably arises from the damping action of the closed coil moving in the magnetic field, *i. e.*, the coil which required 5.5 sec. to move from zero to the end of the deflection had in the most unfavorable instance noted on the curve of Fig. 3 to move during the first 0.4 sec. with the coil closed through the Wheatstone's bridge circuit.

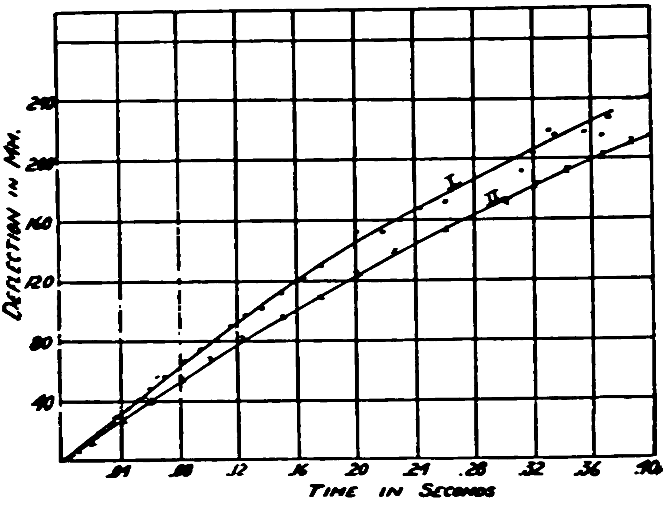

Fig. 3.

Relation between deflection and length of time the galvanometer is in the circuit. I. Galvanometer *E*. Period: 48.8 sec. II. Galvanometer *C*. Period: 22.4 sec.

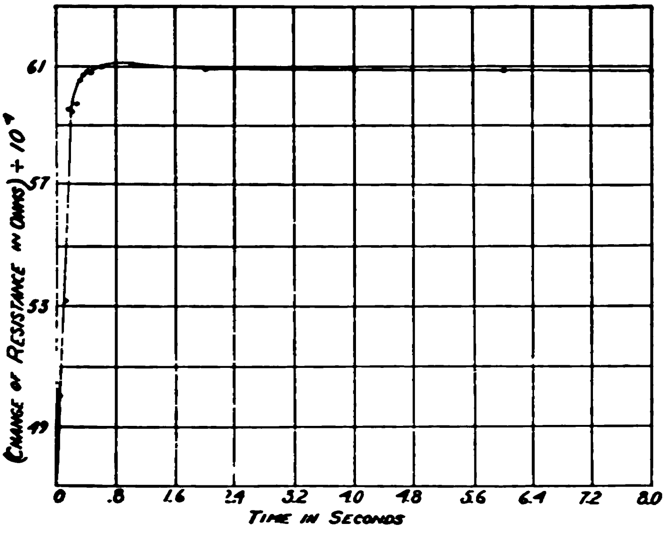

Fig. 4.

Change of resistanace of a Giltay cell with time of illumination. Resistance in the dark 673,000 ohms.

The amount of motion during this time, about one thirteenth of the quarter period, probably damped the coil appreciably. It was quite definitely settled that the linear relation between d and Δt was obeyed for values of Δt as small as .0075 sec. but for values less than this there was considerable doubt. The apparatus used seemed to give deflections consistently too small when Δt was 0.005 sec. It may be stated then that the method suggested for determining changes of resistance is applicable through the use of equation (4) for quite a large range of values for Δx and Δt. The value of the constant C can be computed or determined by experiment. It is hardly necessary to state that the range of applicability will vary to some extent with the apparatus used. There will enter such factors as the sensibility of the galvanometer, the value of the resistances in the circuit, and self-induction.

However, for small variations in resistance it may in practice often be simpler not to compute the change of resistance from the deflection, but to merely substitute known changes in the variable resistance which will give the same deflection that was obtained with the unknown variable resistance, or to obtain enough deflections with known resistances so that the value of the unknown change can be interpolated.

The Measurement of Large Changes of Resistance.—In case the change of resistance, Δx is large compared with the initial resistance x, equation (4) can not be applied and equation (3) is not easily serviceable. The change of resistance is a function of the deflection regardless of how large it may be, but it is not easily computed. We have found the easiest way out of the difficulty to determine the deflections given by the unknown resistance at different intervals of time and then to substitute various known resistances which would give a range of deflection covering those obtained by the unknown. The deflections together with the values of the known resistances were plotted to give a calibration curve. Then the value of the unknown resistance or the change of resistance was read from the calibration curve.

A simple illustration will explain this application of the method. A Giltay selenium cell was connected at x in Fig. 1. The selenium cell was placed in a dark box in which was also a tungsten lamp. By closing both the keys k_3 and k_4 the storage battery circuit was closed through the tungsten lamp. This illuminated the selenium cell. The method of procedure in the experiment was first to balance the selenium cell in the bridge circuit, after it had recovered, and then to set up the keys k_1, k_2, and k_3. Then the key k_4 was closed by hand. When the pendulum was afterward released it closed the key k_3 and illuminated the selenium cell. When the pendulum reached k_1, the galvanometer was thrown in circuit, and when k_2 was reached the galvanometer was thrown out of circuit. The time between k_1 and k_2 gave the interval of time Δt. The time taken for the pendulum to pass from k_3 to the midpoint between k_1 and k_2 was considered the corrected time of exposure of the cell to the light. After the pendulum had thrown the key k_2, the key k_4 was opened by hand. If a period of illumination was desired that was greater than 0.60 sec., the absolute value of the period was not desired so accurately and therefore a crude auxiliary timing pendulum was used. The key k_3 was first thrown by hand and on the second the key k_4 was thrown, thus lighting the selenium and on any desired second the pendulum was released. This method kept the interval Δt constant and gave any period of illumination desired to a sufficient degree of accuracy. If the deflections by this method were too large they were reduced by changing the value of the battery electromotive force or by inserting resistances in series with the battery. Between each reading the selenium was allowed to recover.

The following table gives the observations that were made with the selenium cell.

TABLE.

Corrected Time of Exposure, Sec.	Deflections, mm.	Temperature.	Galvanometer Time Interval.
.05	7	24.8	0.05 sec.
.10	11	24.4	
.20	35	23.8	
.25	38	23.8	
.30	56	23.8	
.35	52	23.8	
.40	55	23.8	
.45	55	23.8	
.60	58	23.8	
1.00	61	23.8	
2.00	57	23.8	
4.00	56	23.8	
6.00	56	23.8	
8.00	55	23.8	

In the above observations the interval that the galvanometer was in the circuit was 0.05 sec. throughout. Using known resistance changes and the same interval 0.05 sec. data were obtained from which was plotted the calibration curve shown in Fig. 5. It will be observed from the calibration curve that for changes of resistance ranging in value from 500,000 to 564,000 ohms the deflection is almost a linear function of the change of resistance. For greater changes however the deflection changes very rapidly and becomes infinite when the change of resistance equals the original resistance in that arm of the bridge. It is interesting to compare this curve with Curve III., Fig. 2. Both are deflection-resistance curves, but in Fig. 2 the change of resistance begins with zero while in Fig. 5 they begin with about 500,000 ohms. The resistances are of entirely different order of magnitude in the two instances.

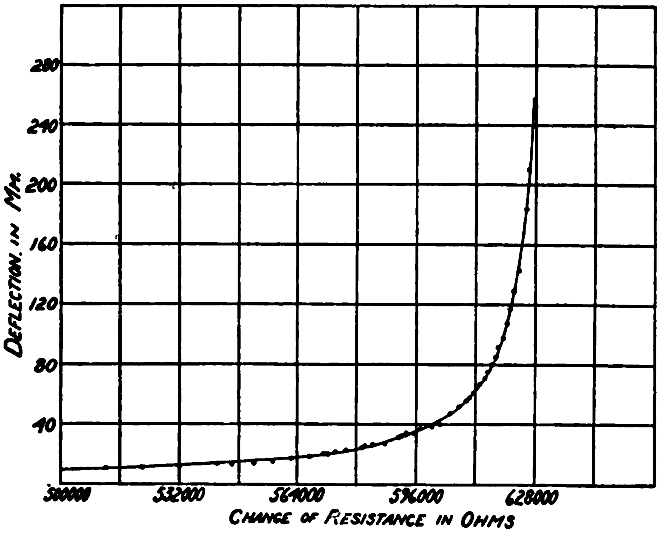

Fig. 5.

Calibration curve showing deflection for various known changes of resistance, when initial or equilibrium resistance is 632,000 ohms. Resistance in the other arms: $R=6320$, $a=1$, $b=100$.

Using the values of the deflection obtained with the selenium cell shown in the accompanying table, we are able to determine the change of resistance from the calibration curve. The magnitude of the change for any time of exposure is shown in the curve of Fig. 4. The points on the curve each represent a single observation. The accuracy of a single observation is greater than we had expected. Almost without exception the points lie on the curve.

Other applications of this method may be found where it is necessary to vary the interval during which the galvanometer is in circuit and also the electromotive force of the battery. It may be stated in conclusion that the method is probably as accurate and as easy to manipulate as any method that has been devised for measuring such rapid fluctuations in resistance.

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INCREASE OF MAGNETIC INDUCTION IN NICKEL BARS DUE TO TRANSVERSE JOINTS.

By E. H. Williams.

THE magnetic properties of very thin layers of iron and of nickel have been studied by Maurain.[1] He showed that these properties are different for the two metals. In the case of iron, the magnetization of very thin layers is much weaker than that of greater masses, whereas, in the case of nickel the opposite is true, that is, thin layers are much more strongly magnetic than thick layers. This difference is no doubt due to a difference in the molecular phenomena of the two metals and has an important bearing on the theory of magnetism.

Ewing and Low[2] have shown that the influence of a plane of transverse section on the magnetic induction of an iron bar is to produce a large magnetic resistance which, however, can be reduced by longitudinal pressure. Now, if the surface layers of nickel are more strongly magnetic than the mass of nickel, it would seem that, in this metal, transverse joints would tend to increase the magnetic induction rather than decrease it as in the case of iron.

In this investigation, the effects of surface layers in bar magnets of iron and of nickel, produced by cutting the bar in planes of transverse section, have been studied and compared under various conditions of field strength and longitudinal pressure.

The apparatus used was similar to that used by Ewing in which a short bar is brought to a condition of endlessness by sinking its ends in a massive yoke of iron which affords an easy path for the return of the lines of induction from end to end. The yoke was in the form of a ring, the outside diameter of which was 17 cm. and its cross-sectional area 24 sq. cm. The length of the primary coil was 8 cm. The samples investigated consisted of a rod of the material 1.27 cm. in diameter, and about 20 cm. long.

The bar was first tested without any cuts, after which it was cut in two in the middle and each end carefully examined to see that it was a plane before being put into contact again. The same tests were again made, several series of observations being taken which agreed with each other very closely. The process was repeated for two and for four cuts.

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[1] Maurain, Jour. de Phys. (4), Vol. 1, p. 151, 1902.

[2] Ewing and Low, Phil. Mag. (5), Vol. 26, p. 274, 1888.

The final results are shown in Tables I. to III., each table being the mean of four or more sets of readings which differed from each other very slightly. In Tables I., II. and III. are given quantities proportional to the magnetic induction. The absolute value of the magnetic induction is larger by the factor 30. It will be noticed that, in the case of iron (Table I.), transverse joints produce a decrease in the magnetic induction in all cases no matter what the value of the pressure or of the magnetic field, while in the case of nickel (Tables II. and III.), for field strengths greater than about 20 or 25 lines per square centimeter, depending on the pressure, the effect of the surface layers of the transverse joints more than counterbalances the effect of the magnetic resistance of the air gap, thus producing an increase in the magnetic induction.

Table I.

Iron. Magnetic Induction B/30.

H	Whole. Compression Kilos per sq. cm.			One Cut. Compression Kilos per sq. cm.			Two Cuts. Compression Kilos per sq. cm.			Four Cuts. Compression Kilos per sq. cm.		
	2	68	135	2	68	135	2	68	135	2	68	135
4	57.6	50.5	47.0	50.7	47.0	44.8	48.1	45.2	42.9	43.2	42.1	39.4
6	121.3	109.5	100.0	107.0	102.9	97.8	102.7	97.7	93.4	86.7	89.5	84.0
10	254.9	234.1	220.4	224.7	216.4	211.8	217.0	215.9	206.0	189.2	194.4	187.1
15	362.3	346.2	335.3	345.4	329.3	327.6	331.9	330.9	320.9	301.7	306.5	297.8
25	454.4	449.7	448.0	444.4	442.8	442.2	441.9	441.8	439.4	426.8	429.3	427.4
50	521.8	522.6	524.4	520.6	521.2	523.6	519.1	521.4	521.3	516.7	517.1	517.7
100	571.9	573.3	575.6	571.2	571.7	574.3	570.6	573.0	573.7	569.6	570.2	572.0
150	603.0	604.0	607.5	602.9	603.3	606.7	603.8	604.7	605.6	601.0	602.2	604.5

Table II.

Nickel—Sample 1. Magnetic Induction B/30.

H	Whole. Compression Kilos per sq. cm.			One Cut. Compression Kilos per sq. cm.			Two Cuts. Compression Kilos per sq. cm.			Four Cuts. Compression Kilos per sq. cm.		
	2	68	135	2	68	135	2	68	135	2	68	135
4	110.1	124.8	132.7	87.1	104.9	116.9	69.4	85.8	97.7	47.4	60.2	70.4
6	123.5	134.8	141.4	107.7	123.7	133.5	93.5	111.1	122.4	69.8	84.1	96.4
10	136.8	145.2	149.6	127.7	139.4	146.6	118.9	132.7	141.2	99.0	114.1	126.1
15	146.8	153.1	156.7	140.9	149.5	155.0	135.6	145.8	152.1	121.7	134.4	144.1
25	159.9	163.7	166.7	157.0	162.6	166.8	154.2	161.1	165.8	147.1	155.6	162.1
50	179.3	181.9	183.4	179.0	182.4	184.4	178.6	182.3	185.2	177.0	181.9	185.1
100	202.3	203.6	203.7	203.0	204.4	205.4	203.3	205.1	206.3	203.9	205.7	207.1
150	216.5	217.2	216.7	216.8	217.5	218.1	217.3	217.9	218.3	217.6	218.1	218.9

An examination of Table I. will show also the Villari effect, that is, for field strengths below a certain value, increase of pressure decreases the magnetic induction, whereas for higher fields, it increases the magnetic induction. For this particular sample of iron the "Vallari critical point" occurs for a field strength between 25 and 50 lines per square centimeter. In another sample investigated it occurred for a magnetizing force considerably less. In the case of nickel (Tables II. and III.), the results, for field strengths up to 150 C.G.S. units or more, show an increase in magnetic induction for increase of pressure, which agrees with the literature on the subject. However, in the case of sample 2 (Table III.), the results indicate a "Vallari critical point" for a field strength between 150 and 200 C.G.S. units. While this effect is not very pronounced, yet the fact that it occurred in each of six series taken with the whole sample leaves no doubt that it exists.

TABLE III.

Nickel—Sample 2. Magnetic Induction B/30.

H	Whole. Compression Kilos per sq. cm.				Two Cuts. Compression Kilos per sq. cm.				Four Cuts. Compression Kilos per sq. cm.			
	2	68	135	210	2	68	135	210	2	68	135	210
4	108.7	113.7	119.0	123.3	67.9	80.3	88.5	95.6	47.0	57.4	66.1	75.0
6	117.4	121.7	126.5	130.4	90.8	103.5	111.2	117.5	68.0	79.9	88.7	96.3
10	127.2	130.8	135.3	138.9	114.7	123.2	129.6	134.5	96.7	108.4	117.2	124.5
15	135.2	138.5	142.6	145.9	128.2	135.4	140.6	145.1	117.6	127.3	134.4	140.5
25	147.5	150.3	153.6	156.7	144.7	150.2	154.8	159.2	140.2	147.5	153.5	158.3
50	169.2	170.7	173.3	175.8	170.6	174.7	177.3	180.8	171.8	176.5	180.1	183.3
100	197.2	197.6	198.7	199.7	200.1	202.0	202.9	204.6	203.3	205.1	206.3	207.3
150	214.6	214.2	214.1	214.5	216.2	217.6	217.6	218.1	218.3	219.1	219.3	219.8
200	227.2	226.0	225.5	225.2	227.3	227.7	227.6	227.5	228.6	229.0	229.0	228.8
250	236.9	235.7	234.7	234.3	236.0	236.9	236.3	236.4	237.3	237.3	236.9	236.8

The effect of transverse sections on the magnetic induction can be best seen by noting the per cent. change of magnetic induction due to these joints. For iron (Table I.), it will be noticed that this is a negative quantity, which indicates that transverse joints in a bar of iron tend always to decrease the magnetic induction by increasing the magnetic resistance. In the case of nickel the results, shown graphically in Figs. 1, 2 and 3, are very different. Beyond magnetic fields of 20 or 25 lines per square centimeter, the per cent. change is a positive quantity, that is, the effect of transverse joints is to increase the magnetic induction. Since the transverse joints produce a number of surface layers, and since, according to the results of Maurain in the article referred to above, these surface layers are much more strongly magnetic than the body of the metal, one would expect to get an increase of magnetic induction provided the effect of the magnetic resistance due to the air-gaps were made less than that of the surface layers by increase of pressure, or the effect of the surface layers were increased by increase of the magnetizing force.

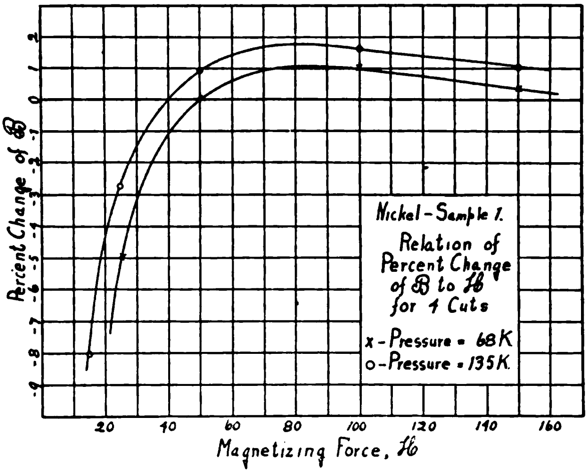

Fig. 1.

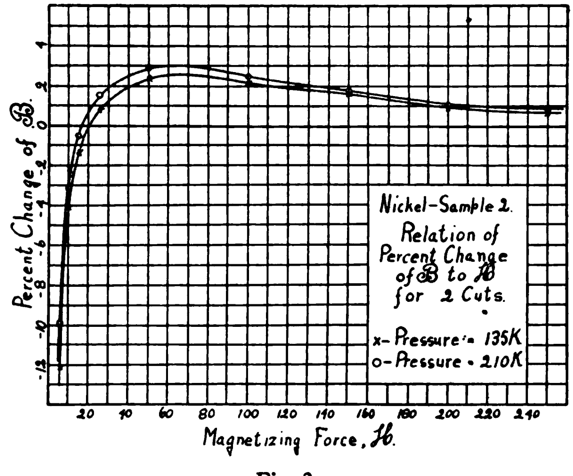

Fig. 2.

Both samples of nickel investigated were very soft as is evident from the comparatively high value of the magnetic induction produced by a magnetizing force of 4 C.G.S. units. Another sample which was very much harder produced little or no increase of magnetic induction due to transverse sections. The value of B in this sample, for a field strength of 4 C.G.S. units, was only about one-third that of the samples given in Tables II. and III.

After the data on sample 1 had been taken and computed, it was noticed that the increase of magnetization reached a maximum value after which it fell off quite rapidly, as is seen from Fig. 1. In order to investigate this point still further, sample 2 was used in which the magnetizing force and pressure were carried to higher values. The same peculiarity was observed as in sample 1. From these results it is evident that the effect of the surface layers is due to two or more causes, and that it does not follow any simple law.

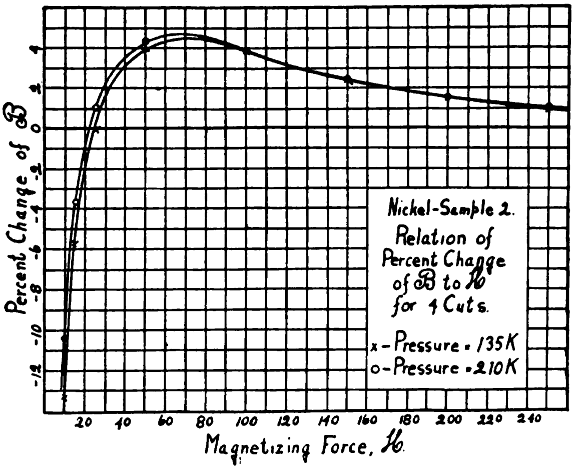

Fig. 3.

That the phenomena observed are molecular phenomena is quite apparent. Now, according to the electron theory, it appears that the elementary magnet of iron consists of two atoms while that of nickel contains six.[1] It is possible that in the surface layers of nickel where the forces binding the molecules together are weaker than in the deeper layers, only four, or even two, atoms form an elementary magnet, thus increasing the number of elementary magnets per unit volume.

In conclusion, I wish to thank Professor Jakob Kunz for suggesting this investigation.

Laboratory of Physics,
University of Illinois,
March 30, 1911.

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[1] Kunz, Phys. Rev., Vol. 30, No. 3, p. 359, 1910.

ON THE FUSION OF CARBON.

By O. P. Watts and C. E. Mendenhall.

In a recent number of the Annalen, LaRosa[1] has described some experiments on the bending of carbon rods at high temperatures and has submitted this bending, together with certain peculiar surface appearances which he observed, as evidence for the existence of a true fusion point for carbon at ordinary pressures. It seemed to the writers that before accepting LaRosa's interpretation of his bending effects it would be well to make further tests with two points especially in mind, namely:

1. To compare the properties of graphite and carbon at high temperatures, to determine whether the bending was due to the traces of binding material (some hydrocarbon) remaining in the carbon, or whether it occurred equally well with graphite, from which the binder might naturally be supposed to have been largely removed by the prolonged and intense heating to which it had been subjected in manufacture.
2. To determine at least approximately the temperatures at which bending occurred, in order to decide whether it really indicated incipient fusion or whether it was merely an evidence of increasing plasticity at high temperatures.

Fortunately we had available a dynamo capable of giving continuously 600 amperes at 110 volts, direct current, so that we could use larger rods than LaRosa, and approach the bending stage gradually, giving ample time for the making of temperature observations on the rod with a Holborn-Kurlbaum type of optical pyrometer. Such observations give directly, of course, only the "black" temperature of the rods; to convert to true temperature we have used results connecting the "black" and "true" temperatures of carbon, shortly to be published by one of us.[2] We have made many tests upon rods 6 mm. in diameter, and 15 cm. and 30 cm. long, the material being (*a*) ordinary commercial carbon made by the National Carbon Co., Cleveland, O., U. S. A.; (*b*) an exceedingly fine-grained high-grade German carbon (Conradty) probably very similar to the material used by LaRosa; and (*c*) the purest graphite made by the Atcheson Graphite Co., Niagara Falls, N. Y. We produced bending either by pushing one electrode toward the other, or by rotating one electrode around a pivot near the center of the rod, or by hanging a weight on two equal rods clamped near to and parallel to each other and connected at their free ends.

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[1] M. LaRosa, Ann. der Physik, No. 1, 1911, p. 95.

[2] Above 2000° C. the determination of this correction requires extrapolation of an empirical curve, so that the highest temperatures may be in error 50 or 75 degrees.

Our results may be briefly summarized as follows:

1. American carbon takes a permanent bend most readily (Fig. 1, No. 3), German carbon next, and graphite with greatest difficulty. This is in the order of increasing purity, and decreasing amount of binding material. Nevertheless we easily obtained even with graphite more pronounced bending than any shown by LaRosa—as for example a sharp bend of 50° in the middle of a 30 cm. graphite rod (Fig. 1, No. 1) produced in four minutes at a temperature between 2700° and 2800° C.

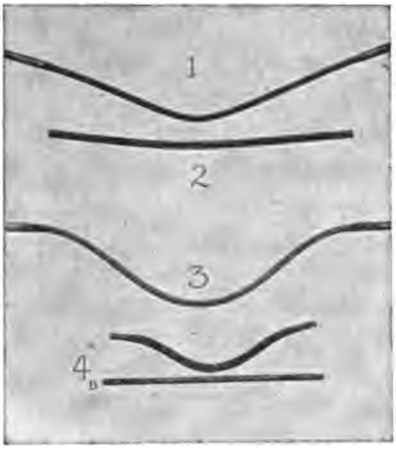

Fig. 1.

No. 1. Graphite. Angle of 50°. Max. temperature = 2770° C.
No. 2. Graphite. Broke hot, while bent 55° at center. 2630° C.
No. 3. Carbon. Angle 75°. Temperature 2600° C.
No. 4A. Rod expanded by carbon vapor. 2900° C.
No. 4B. Original size of rod.

2. The *lowest* temperatures at which bending has been observed are:

For an American carbon rod 1800° C.
For a German carbon rod 1900° C.
For a graphite rod 2150° C.

3. A rod bent while hot will permanently retain a much greater strain if allowed to cool while under stress. This is especially true of graphite, and below 2700° C. For example, one rod was given a 55° bend at 2630° C. in two minutes; it broke while hot and the pieces were almost

straight (Fig. 1, No. 2). Doubtless the *time* under strain will influence the amount of permanent set also. Up to 2500° C. graphite, though viscous as regards slow changes, is quite elastic for rapid changes and a loaded rod will vibrate freely.

4. In attempting to reproduce some of the other phenomena which LaRosa attributed to fusion, namely to obtain fragments of carbon having rounded outlines, and surfaces having a minutely globular structure, we proceeded in two ways: (*A*) Very regular and rather slow heating, obtained by keeping the current constant (about 400 amperes) while the rod or tube slowly diminished in cross section by burning and sublimation; and (*B*) rapid heating, obtained by suddenly throwing on from 300 to 600 amperes, according to the size of rod. In all cases we tried to remove contained gases by preliminary heating to 2000° C. or more.

Case A.—A one-fourth inch carbon rod would run from three to five minutes in the open air, the temperature gradually rising from $T_t = 2500°$ C.; conditions became unstable with considerable regularity at "black" temperatures of 3080° C. to 3250° C. (estimated at 3300° to 3500° C. "true" temperature), and an arc would be formed. The ends of such rods (or tubes) after arcing never presented any appearance of fusion, except that they were sometimes covered in part with a film or coating having a microscopically globular structure such as was described by LaRosa. Such surfaces were found, for example:

1. In the *cooler* parts of the *inside* of a graphite tube, heated to say $T_t = 3100°$ (in a vacuum) at the hottest part. In this case a layer .1 to .3 mm. thick has been *added* to the inside of the tube, reducing the inside diameter. This layer was considerably *harder* and finer grained than the original graphite.

2. On the *center* of the end of graphite rod used as the negative terminal of an arc, the arc playing around the edge of the end.

3. At various times as spots on the end of rod or tube which had arced, but not where the arc had been.

Case B.—Even with careful preliminary heating we frequently obtained violent explosions, undoubtedly due to rapid generation of carbon vapor in the interior of the rod. A further interesting result of this rapid generation of carbon vapor is the very pronounced swelling of carbon rods (less marked with graphite) which occurred with rapid heating (Fig. 1, No. 4). Though the temperature of the surface did not rise above 3000 to 3200° C. (true temperature) the interior was undoubtedly much hotter. A section of such an expanded rod is shown in Fig. 2, No. 1; the center is full of holes and crumbles at the touch, but has no appearance of fusion. A very peculiar effect due to the flow of carbon vapor from the interior of the rod is shown in Fig. 2, No. 2. This nodulated surface presents every appearance of having been fused; yet it is to be noted that such appearances occur only on the outside (and hence cooler) part of the rod; they are more marked with large than with small rods (greater temperature difference between outside and inside); they occur at temperatures several hundred degrees lower than those at which, with slow heating, it has been found possible for a solid carbon or graphite rod to exist. (See above.)

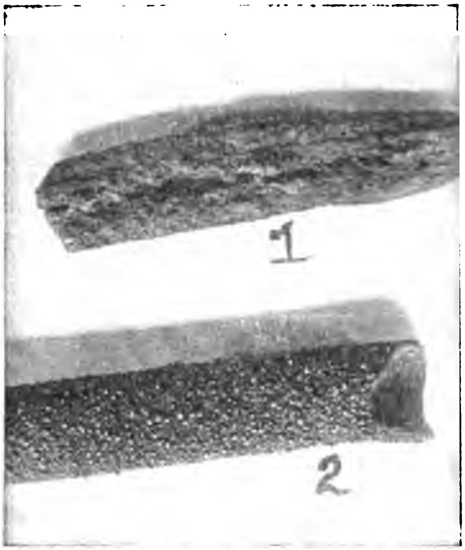

Fig. 2.

Therefore, while the surface appearances described at first sight suggest fusion, we are convinced that they are due in all our cases to condensation of carbon in the relatively cooler regions. The maximum temperature which can be obtained by electrically heating carbon is fixed by the sublimation point at the pressure used. Further increase of energy input after this point is reached simply goes into the energy of sublimination of the carbon. In a vacuum graphite tube furnace at a few millimeters pressure we have obtained in this laboratory a maximum (true) temperature of about 3100° C.; while with a carbon rod in air at 1 atm. pressure we obtained as high as 3500° C. With the same pyrometer a 250 ampere arc gave $T_b = 3500°$ C., or $T_t = 3800°$. The difference between the arc temperature and the highest observed with a rod is undoubtedly the difference between the surface and interior temperature of the rod—the rod breaking down when the *inside* temperature reaches that of the arc.

CONCLUSION.

In view of the above experiments it seems reasonable to conclude that the bending of carbon and graphite at high temperatures cannot of itself be taken as evidence of incipient fusion—but rather as evidence of a gradually increasing plasticity; and while we cannot be sure that the peculiar surface effects observed by us and ascribed to condensation of carbon vapor are the same as observed by LaRosa, still their strong resemblance would lead us to suggest that probably the phenomena described by him were due to condensation and not to fusion.

UNIVERSITY OF WISCONSIN,
April, 1911.

ON THE PRESENCE IN POINT DISCHARGE OF IONS OF OPPOSITE SIGN.

By John Zeleny.

SOME of C. T. R. Wilson's experiments[1] on the action of ions as condensation nuclei indicate that negative ions are present in the gas to which a point is discharging positive electricity; and similar results were obtained by Campbell.[2] Chattock and Tyndall[3] have considered a back discharge from the plane to be a possible explanation for the high values they obtained, from wind pressure, for the mobility of the negative ions in point discharge in pure hydrogen.

The following is an account of some experiments, in which dry air and hydrogen were used at different pressures, that were undertaken to find whether such ions of a sign opposite to that of the main discharge are present, at some distance from the point, in sufficient number to affect the electric field appreciably.

The method is based on the fact that when a wire probe, placed in a gas containing ions, is charged to a higher potential than that which it takes up of itself it cannot return to the latter potential if positive ions only are present, nor can it recover from an imposed lower potential if negative ions alone are present. Any leakage through the gas from a probe wire, placed near a discharging point and charged as stated, must be due to the presence of ions opposite in sign to that of the main discharge.

The accompanying figure shows the arrangement of the apparatus. The wire point B (diameter = .075 mm.) discharged to the plate D (distance = 14.8 mm.) above which the probe wire C (diameter = .26 mm.) was placed, usually at a distance of about 1.5 mm. but in some of the experiments at 6 mm., with like results. This probe wire was charged 200 volts or more above the equilibrium potential assumed by it when a given current was flowing between the point and plane, and its rate of leak noted on a voltmeter joined to it. The rate of leak for a like potential was then taken with no current flowing from the point to test the insulation of the supports.

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[1] C. T. R. Wilson, Phil. Trans., 192, p. 403, 1899.

[2] N. R. Campbell, Phil. Mag. (6), 6, p. 626, 1903.

[3] A. P. Chattock and A. M. Tyndall, Phil. Mag. (6), 19, p. 449, 1910.

No appreciable leak of the probe, that could be ascribed to the ions in question, was observed in dry air at pressures between one atmosphere and half an atmosphere with steady discharge currents of either sign up to 7 microamperes in value, the largest that permitted the taking of observations at these pressures. By comparing the slowest leak detectable with the rate at which the probe assumed the equilibrium potential after being earthed, an estimate was obtained for the upper limit of the number of these ions present and this shows that they must compose less than one fiftieth per cent. of all the ions.

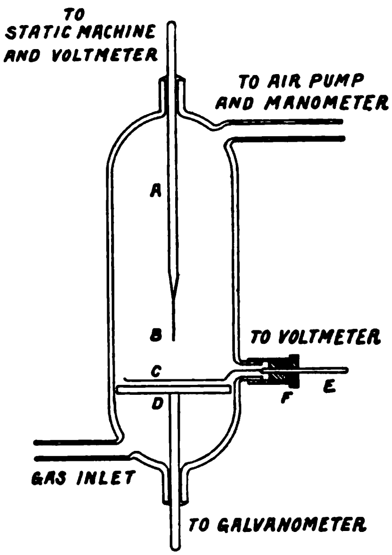

Fig. 1.

Discharge Current in 10^{-6} Amperes.	Rate of Leak from Probe.		
	Negative Discharge.	Positive Discharge.	
0	.08 volts per sec.	.08 volts per sec.	Support insulation leakage.
.4	.25 volts per sec.	.40 volts per sec.	
7.	1.0 volts per sec.	1.6 volts per sec.	
15.	7. volts per sec.	12. volts per sec.	
29.	100±. volts per sec.	very fast.	Glow on plate with negative discharge.

With pressures less than half an atmosphere a leak from the probe was observed; at the higher of these pressures, with large discharge currents only, but with all currents at the lower pressures, of which the lowest used was 3 cm. of mercury.

The preceding set of readings with the air pressure at 17.6 cm. will illustrate the nature of the results. Some idea of the numbers obtained at other pressures may be formed from those given by taking the leakages very roughly inversely proportional to the pressures.

The potential of the probe was in each case over 1,000 volts, and the capacity of the probe and electrometer was about 50 cm. To get an estimate of the relative number of the two kinds of ions present in this case, a capacity was added to the probe system and the rates at which the potential changed were measured when the probe was on the average 250 volts above and below its equilibrium potential. With a positive discharge current of 7 microamperes, for which the potential of the point was 3,600 volts and that of the probe 900 volts, the rate of charging was over 250 times as fast as that of discharging, showing that the ions of opposite sign to the discharge current were less than half a per cent. of the total number present. For the larger currents, however, they were relatively more numerous, as the leakages increase more rapidly than the discharge currents.

It will be noticed that the number of negative ions in the positive discharge is greater than the number of positive in the negative discharge. This is somewhat remarkable since with the largest current used above there was a visible glow on the surface of the plate with the negative discharge and none with the positive. It would seem that this luminosity is not an accompaniment of an ionizing process but may be caused by the impacts of negative ions against the molecules of the gas wherever the ionic velocity is sufficiently great, a potential drop at the surface of the plate being supposed in this case. Such a view would help account for the fact that the light at the surface of a point discharging negative electricity extends some distance into the gas while in positive discharge the light is much more confined to the metal surface.

Observations made at night failed to detect any glow on the surface of the plate when a non-intermittent positive discharge was passing with the gas at any of the pressures used, although with the negative discharge a faint glow was noticed for the largest currents used even when the pressure was as high as half an atmosphere.

In some experiments which were made to see if luminosity may attend recombination, the ions from two points, one discharging positive and the other negative electricity were sent from opposite sides into the space between two earthed gauzes or metal rings but no light effects were seen even with the gas under a greatly reduced pressure.

The results on probe leakage in electrolytic hydrogen were similar to those for air except that the leakages observed were somewhat larger and no glow was observed on the plate for either discharge.

In general then, the experiments show that while at lower pressures and especially in the larger currents there is a considerable number of ions in the gas, of opposite sign to that of the discharge, nevertheless, for pressures down to as low as 15 cm. and with currents up to 7 microamperes at least, these ions are not sufficiently numerous to affect the electric field appreciably.

Physical Laboratory,
University of Minnesota,
March 17, 1911.

NOTES ON OPTICAL PYROMETRY.

By C. E. Mendenhall.

THE following notes describe certain small and rather obvious modifications in existing instruments and methods, which however have been found so convenient that a brief account seems worth while.

1. A convenient mounting for using rotating sectors directly on the Holborn-Kurlbaum pyrometer for cutting down the initial intensity of the light from the hot body, and thus extending the range of the pyrometer. The usual method of accomplishing this is by means of absorbing or reflecting glasses mounted in front of the pyrometer objective, and the determination of the effective absorbing power of the glasses is a matter of some trouble, and it is moreover greatly altered by change in the angle of incidence and by dust. The arrangement of motor, shaft and sectors is clearly shown in Fig. 1; a common battery motor is fixed at the main pivot of the pyrometer, and with a little care in balancing the disc and armature there is no noticeable vibration. The sectors are 13.5 cm. in diameter, and with this size openings as small as 3°, giving a reducing factor of 1/120 for one opening, may be used. It is very easy to have a number of sectors so that any desired reduction may be obtained.

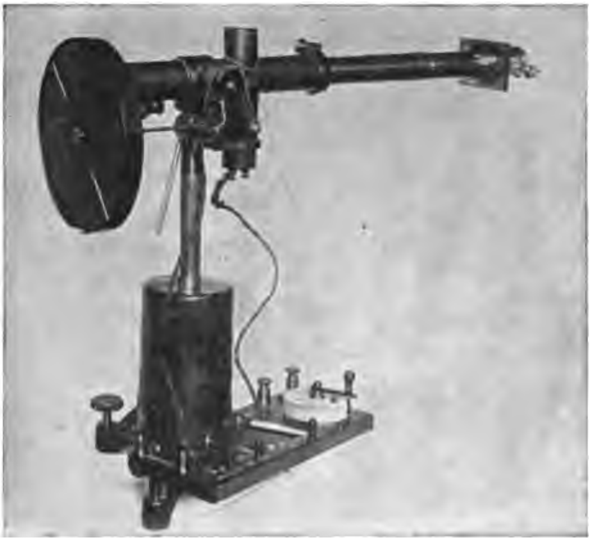

Fig. 1.

2. A method of calibrating the Holborn-Kurlbaum pyrometer using but *one* known temperature and a number of sectors to give a number of reduced effective temperatures. Thus if a black body at the temperature of melting palladium, 1549° C., is used, and observations taken first direct and then with sectors having apertures of ½, ¼, ⅛, 1/20, 1/60, 1/120, corresponding effective temperatures are obtained from about 1450° to 1030° C.

These effective temperatures are calculated from Wien's logarithmic isochromatic, using $C_2 = 14{,}500$ and $\lambda = .658\mu$ as the wave length of effective transmission of the standard red glass used with the pyrometer. The transmission band of this glass is, however, fairly broad, about $.02\mu$, and one naturally raises the question whether the use of Wien's equation (and therefore this method of calibration) is justified, since the equation applies to monochromatic light. We have carefully tested this point in two ways—first by comparison of observations on a black body whose real temperature was 1063° C. (gold point) and on another whose effective temperature, reduced by sectors from 1546° C., was computed to be the same. These observations checked to about 2° C.—which is about the limit of accuracy of ordinary optical pyrometry. A further test was obtained by comparing observations, at various effective temperatures, obtained with the usual red glass eye-piece and with the spectroscopic eye-piece described below. With the latter, having a spectral field of only about $.0025\mu$, the use of Wien's equation is surely justified, and again the agreement was within 2° for the lower temperatures (see table). The sector method of calibrating is therefore justified and its advantages, involving as it does only one steady known temperature, are obvious.

3. A spectroscopic eye-piece for use with the Holborn-Kurlbaum pyrometer. The general form of the eye-piece is shown in Fig. 1; the spectroscopic instrument can be pointed and used just as the ordinary form, using a small auxiliary eye-piece and total reflecting prism which slides in a side tube just back of the lamp. The image of the comparison filament and of the hot surface are thrown in sharp focus across the middle of the spectroscope slit by an intermediate achromatic lens, the primary image of the hot surface having previously been brought into the plane of the comparison filament by focusing in the usual way, using the auxiliary eye-piece. The eye-piece and ocular slit of variable width are movable with a micrometer screw, giving about 500 divisions for the visible spectrum, and it is easy to work with an ocular slit covering not more than 25 A.E. The field then shows a central band due to the filament bordered by light from the hot surface. We have used the instrument very successfully to determine the absolute reflecting power of metallic surfaces. With a few properly chosen sectors, and an intense steady

source of light such as a Nernst glower reflecting powers can be measured to .2 per cent.[1]

The most interesting use of the instrument, however, is to test the validity of the use of Wien's logarithmic isochromatic equation for extending the range of the pyrometer scale, or for calibrating as above described. As pyrometers of the ordinary Holborn type are practically always used with Jena no. 2,745 red glass in the eye-piece to render the transmitted light approximately monochromatic, a comparison through a wide range of temperatures between the readings of the ordinary type (assuming the use of Wien's law to be allowable) and of the spectroscopic type (for which the use of Wien's law is hardly open to question) is of general interest. Our results are given in the table.[2] In computing these results the wave length of effective transmission of the red glass was taken as $\lambda = .658\ \mu$, as determined from spectrophotometric observations. Both instruments were calibrated by the sector method above described using the melting point of palladium as the standard temperature, 1549° C. Within the limits of accuracy which it is ordinarily possible to attain in optical pyrometry the use of Wien's equation in calibration or in extending the scale would therefore seem to be entirely justified.

TABLE.

Temperature, °C. as Determined by: "Red Glass" Pyrometer.	Temperature, °C. as Determined by: Spectroscopic Pyrometer.
1063	1062
1217	1218
1386	1387
1858	1861
1990	1990
2000	1995
2078	2080
2172	2174
2370	2380
2490	2500

SUMMARY.

This paper describes a convenient mounting, method of calibrating and spectroscopic eye-piece for the Holborn optical pyrometer, and gives a comparison of the "spectroscopic" and "red glass" temperature scale which justifies the use of Wien's Law with the ordinary "red glass" form of pyrometer.

UNIVERSITY OF WISCONSIN,
DEPARTMENT OF PHYSICS,
March, 1911.

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[1] Since this instrument was constructed Henning (Zeit. f. Instk., March, 1910) has published a full account of a similar instrument which he also used for measuring reflecting power; this renders a detailed description unnecessary, though it should be mentioned that our form is much simpler than Henning's and can be used and sighted like an ordinary pyrometer.

[2] Observations taken by Mr. Forsythe and Mr. McCauley.

TEMPERATURE COEFFICIENTS OF ELECTRICAL RESISTANCE. III.

By A. A. Somerville.

Two previous articles[1] in the Physical Review have described the apparatus used and its operation and have shown the results obtained in the case of twenty-one materials, most of them being commonly found in a laboratory.

In brief, the apparatus consists of a resistance furnace to heat the specimen, a platinum thermometer in connection with a Callendar temperature recorder to record the temperature of the furnace, a dial bridge to measure the resistance of the specimen, a nitrogen producing plant made by air passing over hot copper and a pump to circulate the nitrogen over the specimen to prevent its oxidation while it is being heated and its resistance is being measured. In each case the material was heated to about 1050° C. unless it melted below that temperature.

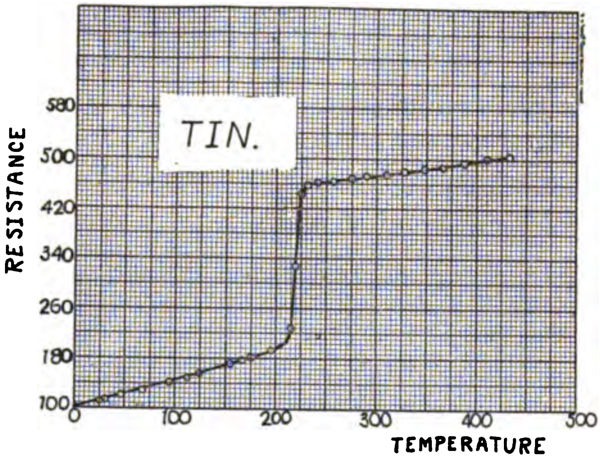

Fig. 1.

During the past year, some of the materials that have been worked with are zinc, tin, german silver, brass, krupp, silicon, phosphor bronze, cupror, climax and monel metal.

[1] Phys. Rev., Vol. 30, No. 4, and Vol. 31, No. 3.

In the case of the pure metals, zinc and tin, having comparatively low melting points, the interesting feature is the change of resistance that takes place when the specimen passes from a solid to a liquid state and vice versa. Another interesting thing about zinc is that if it is drawn into a very fine wire and wrapped in the form of a spiral about a quartz tube the surface tension of the molten zinc is sufficient to hold it together for a considerable further increase in temperature and during this further heating the temperature coefficient of resistance is quite unusual, without doubt being negative and quite uniform for more than 100° before the

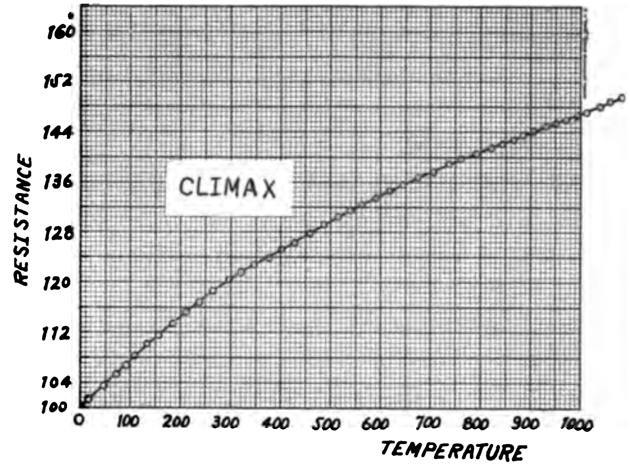

Fig. 2.

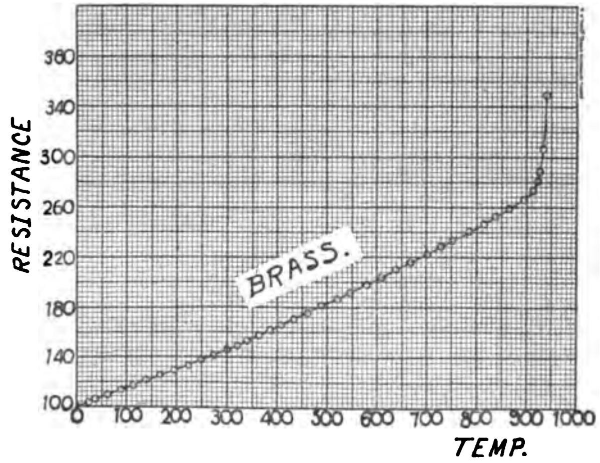

Fig. 3.

thread of zinc pulls apart. On the other hand, if the zinc is drawn into a small quartz tube as a containing vessel and its resistance measured there, the coefficient while in the molten state is almost zero.

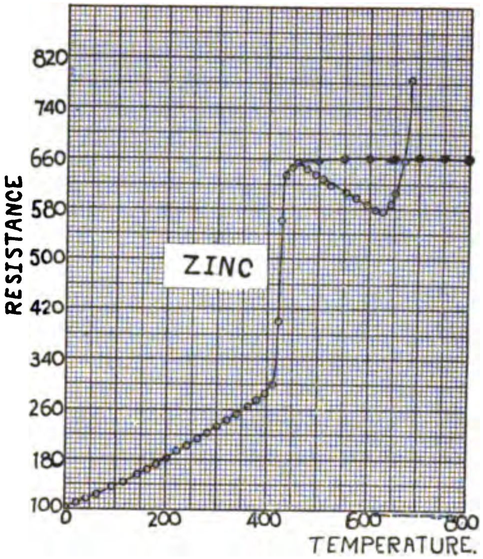

Fig. 4.

The silicon was in the form of rods a few centimeters in length and 2 or 3 mm. in diameter. Connections could be made only by looping wires about a neck ground into either end of the silicon rod and drawing these wires taut by means of weights, so making mechanical rather than

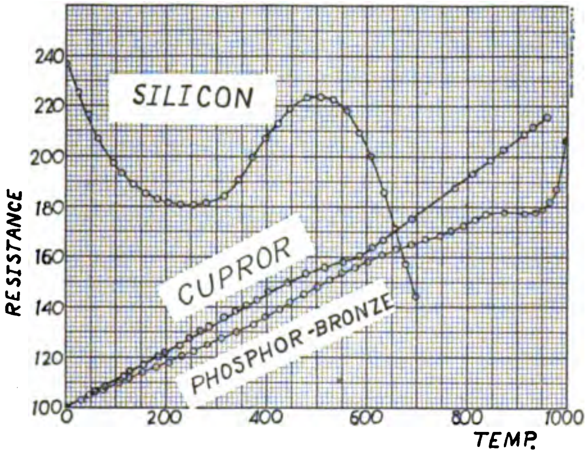

Fig. 5.

electrical contact. Copper plating could not be made to hold lead wires on to the silicon, due to the different expansion of copper and silicon at higher temperatures. The curve shown was readily reproducible.

The other substances are alloys furnished by commercial firms which make claims for their usefulness for various purposes. They are all marked by comparatively low coefficients, as is characteristic of alloys in general, and most of them show marked changes in their coefficients, which is also generally to be expected in alloys.

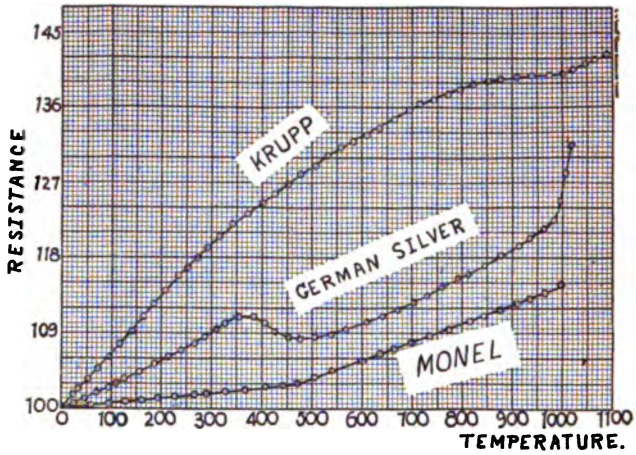

Fig. 6.

Volume XXXIII. *August, 1911.* *Number 2*

THE

PHYSICAL REVIEW.

A VERIFICATION OF THE THEORY OF BROWNIAN MOVEMENTS AND A DIRECT DETERMINATION OF THE VALUE OF *NE* FOR GASEOUS IONIZATION.[1]

BY HARVEY FLETCHER.

INTRODUCTION.

IN 1827 a botanist named Brown noticed that small particles which were suspended in a liquid were in a continual state of agitation; but it was not until 1889 that the correct explanation of this phenomenon was given, when Gouy[2] suggested that it was due to molecular bombardments. In 1905 Einstein[3] deduced a formula which makes it possible to calculate the magnitude of the Brownian displacements. Perrin,[4] Henri,[5] Chandesaignes,[6] and others, working with minute particles suspended in a liquid, obtained results which gave a fair agreement between the calculated and observed values of the displacement. Broglie,[7] who worked with particles of tobacco smoke suspended in air at atmospheric pressure, obtained displacements of the same order of magnitude as given by Einstein's formula.

In the first part of this paper a modification of this formula is proposed, and a new method is given for studying Brownian movements. Formulæ are deduced which give the probable distribution of a great many observed values of:

(1) The displacement of a particle due to Brownian movements.

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[1] A brief summary of this paper was given in Science, February 17, 1911, and a more complete abstract in Phys. Zeit., 12, 1911, pp. 202–208.

[2] Journ. de Phys., T. 7, 1888, p. 561.

[3] Ann. de Phys., 4″ Series, T. XVII., p. 549, 1905.

[4] Le Radium, T. 6, p. 353, December, 1909.

[5] Compt. Rend., T. 146, 1908, p. 1024, and T. 147, p. 65, 1908.

[6] Compt. Rend., T. 147, 1908, p. 1024.

[7] Le Radium, T. 6, p. 203, July, 1909.

(2) The actual displacement in a given time of a particle acted on by a constant force.

(3) The actual time of fall through a fixed distance of a particle acted on by a constant force.

In the second part experimental results are given which verify the equations of Part I., and which make it possible to determine directly the value of Ne for gaseous ionization.

Part I. Theoretical Considerations.

§ 1. *Distribution of the displacements in successive equal intervals of time of a small spherical particle which is under the influence of no outside forces except the impacts of the gas molecules.*

Since the momentum imparted to the particle by the gas molecules is different in different directions, and changes with the time, the displacement in a given time will continually change its direction and magnitude. To find the chance that a displacement between x and $x+dx$ will occur in a time t, let us use an analysis similar to that which was first used by Maxwell to determine the distribution of molecular velocities.

Let $f(x, y, z)dxdydz$ be a function which gives the chance that a displacement lies between (x, y, z) and $(x+dx, y+dy, z+dz)$. As this chance must be the same in all directions, $f(x, y, z)$ must be invariant under a transformation of axes. By a well-known theorem of invariants, we know that the only function satisfying this condition is $f(x^2+y^2+z^2)$, *i. e.*, a function of the radius vector.

If $F(x)dx$ is the chance that the x component of the displacement is between x and $x+dx$, then the chance that the y component is between y and $y+dy$, and that the z component is between z and $z+dz$, is $F(y)dy$ and $F(z)dz$, respectively. Then, assuming[1] that the x component of the displacement is independent of y and z, we have

$$f(x, y, z)dxdydz=f(x^2+y^2+z^2)dxdydz=F(x)dx\cdot F(y)dy\cdot F(z)dz.$$

Solving,

$$f(x^2)=A^2F(x),\ f(y^2)=A^2F(y),\ f(z^2)=A^2F(z),$$

where

$$A=F(0).$$

Then

$$f(x^2+y^2+z^2)=\frac{1}{A^6}f(x^2)\cdot f(y^2)\cdot f(z^2).$$

Substitute

$$\log\left\{\frac{1}{A^3}f(x^2)\right\}=H(x^2).$$

---

[1] Boltzman objected to a similar assumption in Maxwell's work, but obtained the same formula by a more rigorous analysis.

Then

$$H(x^2+y^2)=H(x^2)+H(y^2).$$

Therefore

$$H(x^2)=-\alpha x^2$$

and

$$H(y^2)=-\alpha y^2$$

and our required solution is

$$f(x,\ y,\ z)=A^3e^{-a(x^2+y^2+z^2)}. \tag{1}$$

Also

$$F(x)dx=Ae^{-\alpha x^2}dx,\quad F(y)dyAe^{-\alpha y^2}dy,\quad F(z)dz=Ae^{-\alpha z^2}dz. \tag{2}$$

As (2) gives the probability that a displacement lies between x and $x+dx$, then, if η displacements of a single particle are observed, the number which will probably lie between x_1 and x_2 is given by

$$n=\eta\int_{x_1}^{x_2}Ae^{-\alpha x^2}dx. \tag{3}$$

A and α are functions which are independent of x, and are determined by the equations:

$$\eta=\eta A\int_{-\infty}^{\infty}e^{-\alpha x^2}dx=A\eta\sqrt{\frac{\pi}{\alpha}}$$

and

$$(x^2)_a{}^{*}=A\int_{-\infty}^{\infty}x^2e^{-\alpha x^2}dx=A\tfrac{1}{2}\alpha^{-\frac{3}{2}}\sqrt{\pi},$$

which give

$$A=\sqrt{\frac{\alpha}{\pi}}, \tag{4}$$

$$\alpha=\frac{1}{2(x^2)_a}. \tag{5}$$

It is plain that we can interpret η in the above formula as referring to η similar particles having displacements in one and the same interval of time t, and the same analysis will hold. With such an interpretation $(x^2)_a$ is a group average, that is to say, all the particles having displacements between o and Δx are taken in one group: those between Δx and $2\Delta x$ in a second group, and so on. It seems reasonable to suppose that the average square of the displacement during a time t of η similar particles obtained in this way is the same as the average square of the displacement of one single particle during η successive intervals of time t, and this supposition will be made in what follows.

The average displacement along any axis is zero, but the average

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[*] In this work the subscript a has been used to denote an average value, and the subscript p to denote the most probable value.

absolute value of the displacement, that is, the average of the positive or negative displacements is

$$(6)\qquad x_a = 2\sqrt{\frac{\alpha}{\pi}}\int_0^\infty xe^{-\alpha x^2}dx = \sqrt{\frac{2}{\pi}}\sqrt{\overline{(x^2)}_a}.$$

In order to find the absolute displacement in space, change $f(x, y, z)$ in (1) to spherical coördinates by the transformations

$$r^2 = x^2+y^2+z^2;\quad x = r\cos\theta;\quad y = r\sin\theta\cos\varphi;\quad z = r\sin\theta\sin\varphi.$$

Then the number out of η displacements that lie between r and $r+dr$ is

$$dn = \eta\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} r^2e^{-\alpha r^2}dr\int_0^{2\pi}d\varphi\int_0^\pi \sin\theta d\theta,$$

or

$$(7)\qquad dn = \eta 4\pi\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} r^2e^{-\alpha r^2}dr.$$

This function has a maximum at $\alpha r^2 = 1$. Therefore the most probable displacement is given by

$$(8)\qquad r_p = \sqrt{2}\sqrt{\overline{(x^2)}_a}.$$

The average displacement in space is

$$(9)\qquad r_a = 4\pi\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int_0^\infty rr^2e^{-\alpha r^2}dr = 2\sqrt{\frac{2}{\pi}}\sqrt{\overline{(x^2)}_a}.$$

which shows that $r_a = 2x_a$.

It is also useful for comparison with observation to find an expression for the average displacement in a plane. The chance that the projection of the displacement on the xy plane is between (x, y) and $(x+dx, y+dy)$ is $F(x)dx\cdot F(y)dy$, or

$$\frac{\alpha}{\pi}e^{-\alpha(x^2+y^2)}dxdy.$$

Now transform by the relations

$$x = R\cos\theta \text{ and } y = R\sin\theta,$$

and we get for the number out of η displacements that lie between R and $R+dR$

$$dn = \eta\frac{\alpha}{\pi}Re^{-\alpha R^2}dR\int_0^{2\pi}d\theta,$$

or

$$(10)\qquad dn = 2\eta\alpha Re^{-\alpha R^2}dR.$$

This shows a maximum at $\alpha R^2 = ½$, or the most probable value of the displacements in a plane is

$$R_p = \sqrt{(x^2)_a}. \tag{11}$$

The average projection of the displacement on a plane is

$$R_a = 2\alpha \int_0^\infty R^2 e^{-\alpha R^2} dR = \sqrt{\frac{\pi}{2}(x^2)_a}. \tag{12}$$

So we see that if the value of $(x^2)_a$ can be determined, the distribution of the displacements, the average and most probable values of the displacements along an axis, in a plane, or in space can be calculated.

§ 2. *Resistance offered by a gaseous medium to a spherical particle moving uniformly through it.*

Before obtaining an expression for $(x^2)_a$ from dynamical considerations, it is necessary to consider the law of motion of a small particle moving through the gas. Stokes gave an approximate solution to this problem by starting from the fundamental equations of hydrodynamics. However, in solving, it was necessary to make the following assumptions and approximations.

1. A continuous medium.
2. An incompressible fluid.
3. Uniform density.
4. No impressed force upon the gas.
5. The mathematical approximation that the square of the velocity of the gas at any point is negligible.
6. No slip at the surface of the particle.

If F is the force acting upon a particle of radius a, moving with a constant velocity v, through a gas whose coefficient of viscosity is μ, then, with the above assumptions,

$$F = 6\pi\mu a v. \tag{13}$$

If we assume that there is external friction at the surface of the particle, the hydrodynamical[1] equations show that

$$F = 6\pi\mu a k' v, \tag{14}$$

where

$$k' = \frac{1 + \frac{2\mu}{\beta a}}{1 + \frac{3\mu}{\beta a}}, \tag{15}$$

β being the coefficient of external friction. Or, if the coefficient of slip, defined by the equation

$$\rho = \frac{\mu}{\beta}$$

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[1] Bassett's Hydrodynamics.

be introduced,

$$k' = \frac{1 + 2\frac{\rho}{a}}{1 + 3\frac{\rho}{a}},$$

and if we can neglect $(\rho/a)^2$ in comparison to ρ/a,

$$k' = \frac{1}{1 + \frac{\rho}{a}}. \tag{16}$$

In order to take account of the molecular structure of the gas, Cunningham[1] has modified Stokes's formula by considering the impacts of the gas molecules upon the particle and has deduced from the theory of probability that

$$F = 6\pi\mu akv, \tag{17}$$

where[2]

$$k = \left(1 + \frac{\frac{3}{2}\frac{l}{a}}{f - 2(f - 1)}\right)^{-1}, \tag{18}$$

l being the mean free path of the gas molecule, and f the fraction of the total number of impacts which are elastic. Experiments[3] on oil drops suspended in air at atmospheric pressure show that, at least for the range investigated, if f is put equal to zero, this formula agrees fairly well with the experimental results. Then (18) reduces to

$$k = \frac{1}{1 + \frac{3}{4}\frac{l}{a}}. \tag{19}$$

It is seen that these two formulæ become the same if we place

$$\rho = \tfrac{3}{4}l.$$

From considerations of the kinetic theory, Meyer[4] has deduced the formula for the coefficient of slip

$$\rho = \frac{4}{B}0.3097l,$$

where B is a number between 0 and 2 depending upon the loss of velocity of the molecule upon hitting the surface of the particle. Maxwell[1] gives for the inelastic case

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[1] Proc. Roy. Soc., Vol. A 83, No. A 563, 1910, page 357.

[2] See note 3, page 380, PHYS. REV., April, 1911.

[3] Millikan, PHYS. REV., April, 1911.

[4] Meyer, Die Kinetische Theorie der Gase, p. 211.

$$\rho = \tfrac{2}{3}l.$$

So we see that either Basset's hydrodynamical formula or Cunningham's probability formula is sufficient to represent the experimental facts as long as l/a is small compared to 1. But when l/a becomes greater than 1, they are very different, for in the former k always lies between 1 and $\tfrac{2}{3}$, while in the latter, k lies between 1 and 0.

In either case, if m is the mass of the particle, then its velocity of steady fall is

$$v = \frac{mg}{6\pi\mu ak}.$$

§ 3. *The average square of the displacement due to molecular impacts.*

If X is the x component of the forces due to the unbalanced molecular impacts of the gas molecules, then the equation of motion along the x axis is

$$m\frac{d^2x}{dt^2} = -F + X,$$

or

$$m\frac{d^2x}{dt^2} = -6\pi\mu ak\frac{dx}{dt} + X. \tag{21}$$

Multiply by x and substitute $d(x^2)/dt = z$, and $dx/dt = v$ and we get

$$\frac{m}{2}\frac{dz}{dt} + 3\pi\mu akz = mv^2 + Xx.$$

If η similar equations are written representing the motion at the same instant of time of η similar particles, then grouped and averaged as indicated in § 1 there results

$$\frac{m}{2}\frac{dz_a}{dt} + 3\pi\mu akz_a = \frac{m}{\eta}\sum_1^\eta v_n^2 + \frac{1}{\eta}\sum_1^\eta X_n x_n.$$

It is obvious that when η is very large

$$\sum Xx = 0,$$

as then there would be a group of particles having a negative $X_n x_n$ for every one having a positive $X_n x_n$. Also, since the average kinetic energy of a single particle taken over a long period of time may be taken to be the same as the average kinetic energy of a great many similar particles at any instant of time, $\frac{1}{2}\frac{m}{\eta}\sum_1^\eta v_n^2$ is equal to the average energy of translation in the direction of x of any one of the particles during a long interval of time. If ϵ is the average energy of agitation of the gas molecule and we assume that, on the average, this energy is distributed equally among three rectangular components; then, according to the law of equal partition of energy,

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[1] Maxwell's Scientific Papers, Vol. II., p. 709.

$$\frac{1}{2}\frac{m}{\eta}\sum_{1}^{n} v_n^2 = \frac{1}{3}\epsilon. \tag{22}$$

With these assumptions (21) reduces to

$$\frac{m}{2}\frac{dz_a}{dt} + 3\pi\mu a k z_a = \frac{2}{3}\epsilon,$$

the solution of which is

$$z_a = \frac{2}{3}\epsilon\frac{1}{3\pi\mu a k} + Ae^{-\frac{6\pi\mu a k t}{m}}.$$

The last term is negligible for any time large enough to measure. Therefore,

$$(x^2)_a = \frac{2\epsilon t}{9\pi\mu a k}, \tag{23}$$[1]

where the displacement is measured from the origin.

It is plain from the manner in which the formula for $(x^2)_a$ was derived that it represents the average square of the displacement along the x axis during a time t of a larger number of similar particles, which is taken as the same as the average square of the displacement of a single particle during a larger number of successive equal intervals of time t.

Since $\sum Xx$ necessarily oscillates about zero as n increases it will not only be negligible for n infinite but for many finite values of n and for each of these a solution similar to (23) would be obtained, but the coefficient of t, in general, would be different. Physically, this only means that the average of one series of displacements would not be exactly the same as that of another unless the two series contain an infinite number of displacements.

If the value of $(x^2)_a$ is placed in the formula deduced in § 1, we have the following six forms giving the magnitude of the Brownian displacement.

$$\sqrt{(x^2)_a} = \sqrt{2}K, \tag{23'}$$ $$r_a = \frac{4}{\sqrt{\pi}}K, \tag{9'}$$

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[1] This formula was first deduced by Einstein (Ann. d. Phys., 17, p. 559, 1905) and given in essentially the same form as above by Langevin (Compt. Rend., 146, 1908, p. 530). The factor k was not in their formulæ.

$$(6') \qquad x_a = \frac{2}{\sqrt{\pi}} K, \qquad\qquad (11') \qquad R_p = \sqrt{2} K,$$

$$(8') \qquad r_p = 2K, \qquad\qquad (12') \qquad R_a = \sqrt{\pi} K,$$

where

$$K^2 = \frac{\epsilon t}{9\pi\mu a k}.$$

§ 4. *Effect of Brownian movements upon a small spherical particle moving under the influence of a constant outside force.*

Let the actual displacement be divided into two parts, that due to gravity, and that due to the Brownian movements. The former is simply Vt, where V is a constant, and t is the displacement in one second or the velocity due to gravity. The latter on the average is proportional to the square root of t [see (23)]. In order to treat the problem mathematically it will be assumed that each single displacement due to the Brownian movements may be represented by (24)

$$(24) \qquad x = u\sqrt{t},$$

u, the displacement in one second due to the Brownian movements, being independent of the time, and varying in different observed values of the displacement in such a way as to give x a distribution represented by (3). This assumption, which amounts to replacing the perfectly disorganized system by a more regular system which has the same distribution and average value of the displacement, seems reasonable, and the results to which it leads may be checked by experiment.

If the value of x from (24) and the value of α from (5) and (23) is substituted in (3), we obtain an expression for the distribution of the values of u, namely

$$(25) \qquad u = \eta \sqrt{\frac{h}{\pi}} \int_{u_1}^{u_2} e^{-hu^2} du,$$

where

$$(26) \qquad h = \frac{9}{4} \frac{\pi\mu a k}{\epsilon}.$$

The average value of u is given by

$$u_a = 2\sqrt{\frac{h}{\pi}} \int_1^{\infty} u e^{-hu^2} du = \sqrt{\frac{1}{\pi h}},$$

or

$$(27) \qquad u_a = 3\sqrt{\pi}\sqrt{\frac{\epsilon}{\pi\mu a k}},$$

which is the same as (6) for $t = 1$, as it should be. Then, if the total displacement is designated by b, we have

$$b = Vt + u\sqrt{t}. \tag{28}$$

To obtain an expression for the distribution of the total displacements in a fixed time, we treat V and t in (28) as constants and by means of this equation change the variable in (25) from u to b. We get for the number out of η displacements that lie between b_1 and b_2

$$n = \eta\sqrt{\frac{h}{\pi t}}\int_{b_1}^{b_2} e^{-\frac{h}{t}(b-Vt)^2}db, \tag{29}$$

$$b_a = \sqrt{\frac{h}{\pi t}}\int_{-\infty}^{\infty} be^{-\frac{h}{t}(b-Vt)^2}db = Vt. \tag{30}$$

This last result could have been obtained directly from (28), since t is constant and the average value of u is zero.

Similarly, to obtain an expression for the distribution of the times of fall through a fixed distance, we treat V and b as constants and change the variable from u to t and obtain for the number of times of fall which lie between t_1 and t_2

$$n = -\eta\sqrt{\frac{h}{\pi}}\int_{t_1}^{t_2}\frac{bt^{-\frac{3}{2}} + Vt^{-\frac{1}{2}}}{2}e^{-\frac{h}{t}(b-Vt)^2}dt,$$

or, putting $t_g = b/V$ and reversing the limits,

$$n = \frac{\eta V}{2}\sqrt{\frac{h}{\pi}}\int_{t_2}^{t_1}(t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}})\, e^{-\frac{h}{t}(b-Vt)^2}dt. \tag{31}$$

Solving (28) for $\sqrt{t}$ we get

$$\sqrt{t} = \frac{-u + \sqrt{u^2 + 4bV}}{2V},$$

which shows that the limits corresponding to

$u_1 = -\infty$ and $u_2 = \infty$ are $t_1 = \infty$ and $t_2 = 0$ respectively.

Therefore,

$$1 = \tfrac{1}{2}V\sqrt{\frac{h}{\pi}}\int_{0}^{\infty}(t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}})\, e^{-\frac{h}{t}(b-Vt)}dt,$$

and

$$t_a = \tfrac{1}{2}V\sqrt{\frac{h}{\pi}}\int_{0}^{\infty} t(t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}})\, e^{-\frac{h}{t}(b+Vt)}\, dt = \sqrt{\frac{h}{\pi}}\int_{-\infty}^{\infty} te^{-hu^2}du,$$

or, substituting the value of t in terms of u,

$$t_a = \sqrt{\frac{h}{\pi}} \int_{-\infty}^{\infty} \frac{2u^2 + 4bV - 2u\sqrt{u^2 + 4bV}}{4V^2} \cdot e^{-hu^2} du,$$

which gives

$$(32) \qquad t_a = \frac{1}{4hV^2} + \frac{b}{V},$$

or, solving for V,

$$(33) \qquad V = \frac{b}{t_a}\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{t_a}{hb^1}}\right) \underset{\cdot}{=} V_a\left(1 + \frac{t_a}{4hb^2}\right),$$

$$(34) \qquad t_g = t_a\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{t_a}{hb^2}}\right)^{-1} \underset{\cdot}{=} t_a\left(1 - \frac{t_a}{4hb^2}\right).$$

These formulæ show that, although the average of a great many observed distances of fall during a fixed time is the actual displacement due to gravity, the average of a great many times of fall through a fixed distance is somewhat different from the time of fall due to gravity. The difference, if small, is inversely proportional to the square of the fixed distance.

The value of the integral in (31) may be obtained by graphical means, or preferably from an error function table, since

$$\eta\sqrt{\frac{h}{\pi}} \int_{t_2}^{t_1} \frac{V}{2}(t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}})\, e^{-\frac{h}{t}(b-Vt)^2} dt = \eta \frac{1}{\sqrt{\pi}} \int_{s_1}^{s_2} e^{-s^2} ds,$$

where

$$s = \sqrt{h}\,\frac{b - Vt}{\sqrt{t}}.$$

All of the equations in this section can be applied to a particle under the influence of constant forces other than gravity, as for example, a charged particle in a uniform electric field. In this paper V', t', t_a', t_b', etc., will be used in place of the letters given above when they refer to a particle charged with a single elementary charge under the combined influence of gravity and a uniform electric field. Similarly, V'', t'', and V''', t''', etc., will refer to a particle charged with 2, 3, etc., elementary charges.

§ 5. *Effect of Brownian movements upon the apparent value of the electric charge carried by a particle suspended in a gas.*

The method of measuring e which was originated by Professor Millikan[1] consists in getting an isolated charged particle between two condenser plates and observing its velocity V_1 under the influence of gravity, and then its velocity V_1' when the electric field is on. If E is the strength of the electric field in absolute electrostatic units acting upon the particle of apparent mass m' and density σ; g, the gravitational constant; and ρ, the density of the gas, then the following three equations enable one to express the value of e, the electric charge carried by the particle in terms of measurable quantities.

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[1] Phil. Mag., February, 1909; Science, p. 436, September 30, 1910; Phys. Zeit., No. 24, December, 1910.

$$\frac{Ee + m'g}{m'g} = \frac{V_1'}{V}, \tag{35}$$

$$6\pi\mu a k V_1 = m'g, \tag{20'}$$

$$m' = \tfrac{4}{3}\pi(\sigma - \rho)a^3. \tag{36}$$

Eliminating m' and a and solving for e we get

$$e = 9\sqrt{2}\pi\sqrt{\frac{(\mu k)^3}{2(\sigma - \rho)}}\cdot\frac{V^{\frac{1}{2}}(V^1 - V_1')}{E}. \tag{37}$$

(35) and (20′) are derived on the assumption that Ee and $m'g$ are the only forces acting upon the drop, in other words, that the X spoken of in § 3 is zero. This is never strictly true, and therefore the observed velocities are variables, even for a particle which does not change its size, shape or the electric charge which it carries. However, (31) shows that the successive times of fall through a distance greater than 1 cm. of a particle having a radius larger than 100×10^{-6} cm., suspended in air at atmospheric pressure, differ from t_g by less than one tenth of a second. In any case, if V and V' are substituted in place of the observed velocities V_1 and V_1', the value of e should be correct and invariable.

PART II. EXPERIMENTAL APPLICATIONS.

§ 1. *Description of apparatus and method of observation.*

The apparatus which was used in these experiments was designed by Professor Millikan and the writer for the sake of testing the laws of motion of a small drop through a gas at reduced pressures; the results of this study are to be published in another paper. As will appear later, the results herein contained are completely independent of these laws. The same condenser plates which were described by Professor Millikan[1] were placed in a brass vessel which could be made air tight. The arrangement is represented in the vertical cross section in Fig. A. D_1 and D_2 represent the condenser plates. M_1 is an electro-magnet which slides the cover F off of a small hole which is bored through the top plate. M_2 is another electro-magnet which lifts the lead screen L, thus exposing the air chamber between the condenser plates to the ionizing effect of a few milligrams of radium bromide. *A* is an ordinary atomizer. B_1, B_2 and B_3 are ebonite bushings through the walls of the brass cylinder. *P* represents a pump which may be used either for exhaustion or compression. *G* is a high pressure gauge and *H* is a low pressure gauge or simply a U-shaped manometer. All of the air which goes into the brass vessel is made to pass through a vessel *N* which contains glass wool moistened with sulphuric acid. Also the interior of the large vessel is thoroughly oiled, so that the air with which the atomizer is blown and also the air contained in the vessel is dry and dust-free. C_1, C_2, C_3, C_4, C_5 and C_6 are ordinary stop cocks. The enclosing brass cylinder is connected by means of the binding post *T* through the resistances R_1, 20 ohms, and R_2, 450 ohms, to earth. The switch S_3, when in contact with the mercury cup *r*, short circuits the two plates D_1 and D_2 and connects them to earth, and when in contact with the mercury cup *l*, produces an electrostatic field between the plates, the intensity of which is measured by the voltmeter *V*. *K* represents a commutator. The knife edge double pole switches S_1 and S_2 operate the electro-magnets M_1 and M_2 respectively.

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[1] PHYS. REV., April, 1911.

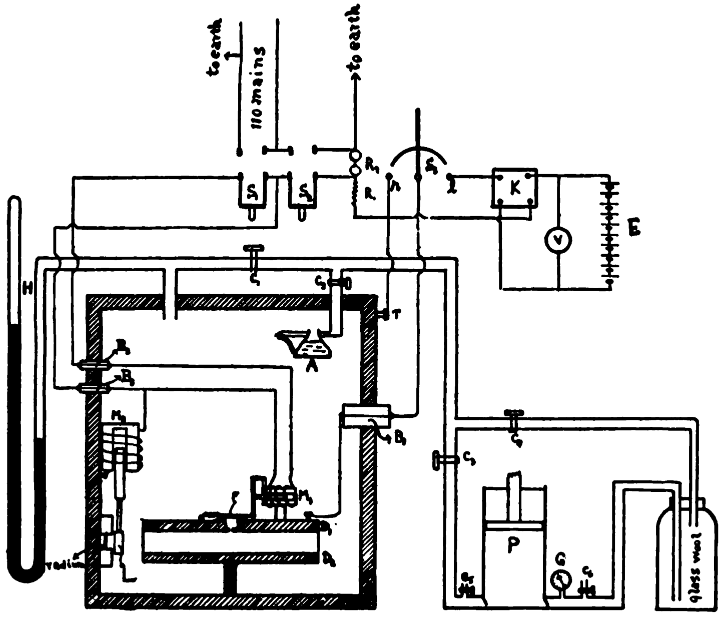

Fig. A.

The horizontal cross section in Fig. B shows the method which was used to illuminate the small oil droplet. Light from an electric arc *A* is made very slightly convergent by a plano-convex lens *L*, and then passes through a column of water 40 inches long which absorbs practically all of the radiant heat. To prevent the light from falling upon either plate it is passed through a slit *s* before entering the large cylinder, and then through the plane glass windows W_1 and W_4, falling upon the oil drop near the center of the plate. The illuminated oil drop is observed through the telescope *T* which is placed at an angle of about 172° with the incident beam. A scale with seven large divisions subdivided into tenths is placed at the focus of the objective and viewed by the eye-piece. The screen *MN* serves to cut off all of the light and heat from the arc except when an observation is being taken.

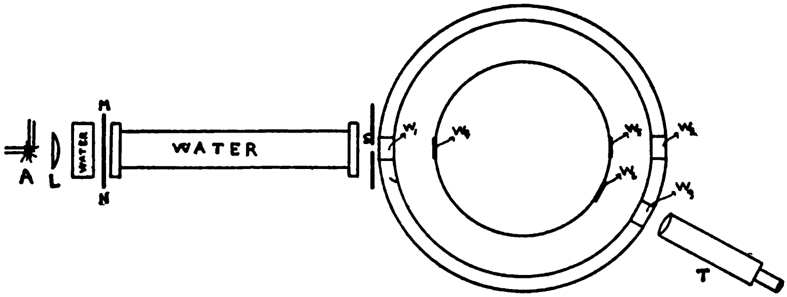

Fig. B.

To take a set of observations, C_1, C_2 and C_6 (Fig. A) are opened, and the air is exhausted from the large vessel until the manometer *H* shows the desired pressure. Then these stop-cocks are closed and C_4 and C_5 are opened and the air is compressed in the vessel *N*. The cover *F* is removed by closing the switch S_1; C_3 is opened, and the atomizer produces a fine oily spray which falls through the small hole in the top plate, and which finally comes between the condenser plates into the beam of light, where it can be seen by the aid of the telescope. In this spray of oil the individual drops differ very much in size and the magnitude of the charge which they carry—the smaller showing strong Brownian movements while the larger ones are almost wholly unaffected. Since they would then have different velocities both in the gravitational field and electrostatic field it is possible to select any desired droplet and keep it in the field of view; and, at the same time, rid the field of all the others.

If at any time the droplet should become uncharged and continue to fall after the electrostatic field is turned on, the lead screen *L* is lifted by closing the switch S_2, thus permitting the radium to produce ions in the space between D_1 and D_2, some of which are soon caught by the droplet. By adjusting the strength of the field, the droplet may be balanced, or made to move up or down with any speed that is desired. In this way small drops which have shown strong Brownian movements have been held under observation for more than five hours, in which time as high as 411 times of fall or displacements have been taken upon the same drop.

In order to calculate what the distribution of the times of fall or displacements should be, it is necessary to know the value of h. If m' is eliminated from (35) and (20′) we have

$$ak = \frac{Ee}{(V + V')6\pi\mu}, \tag{38}$$

or substituting this value in (26) and remembering that

$$\epsilon = \frac{3}{2}\frac{RT}{N},$$

there results

$$h = \frac{1}{4}\frac{Ne}{RT}\cdot\frac{E}{(V + V')}, \tag{39}$$

and

$$u_a = 2\sqrt{\frac{RT}{\pi Ne}}\sqrt{\frac{V + V'}{E}}. \tag{40}$$

This shows that *all the distributions spoken of in Part I., and also the average value of the Brownian displacement in one second can be calculated without knowing the density of the drop, the viscosity or pressure of the gas, or the law of motion of a sphere through a viscous medium. The only assumption involved is that the velocity of steady motion is proportional to the moving force*, an assumption which is fully justified experimentally both here and elsewhere. To obtain u_a and h it is only necessary to know the electrostatic field strength, the velocity of the drop in this field when it carries a single elementary charge, and its velocity when the condenser plates are short-circuited. It is very easy to tell what velocity in the electric field corresponds to a single elementary charge, as has been explained elsewhere.[1] Since Ne/RT is known very accurately, the error in the calculated values of h and u_a depends only upon the accuracy with which E and $V + V'$ can be measured. Therefore at the beginning of each set of observations 10 or 20 times of fall and times of rise through a long distance are taken, which determine V and V' very accurately. Even though V is so small as to be materially affected by the Brownian movements, V' can always be made so large that the error in the average of 10 or 20 values of $V + V'$ is small.

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[1] Millikan, Phys. Rev., April, 1911. Millikan and Fletcher, Phil. Mag., July, 1911.

§ 2. *Comparison of the observed and calculated values of the Brownian displacement in a fixed time.*

To observe directly the component of the Brownian displacement along a line, the value of Xe was made equal and opposite to mg so that on the average the drop travelled neither up nor down. The vertical distance of the drop from some reference line in the eyepiece was noted every 10 seconds. Then the difference in two consecutive readings gives directly the Brownian displacement. Table I. shows the results obtained for a single oil drop. In the first part are the data which determine V and V'; in the second part the displacements are arranged not in the order in which they were observed but according to their magnitude. In the last part "obs n" is the number of these displacements which lie between x_1 and x_2 and "cal n" is the value of n obtained from (3). The comparison between "obs n" and "cal n" is shown graphically in curve 1 (Fig. 1). The smooth curve is obtained by plotting values of $\eta\sqrt{\frac{\pi}{\alpha}}e^{-\alpha x^2}$ as ordinates and x as abscissas, while the broken curve is obtained from values of "obs n" in Part III. of Table I. The abscissas are expressed in terms of the eye-piece scale divisions.

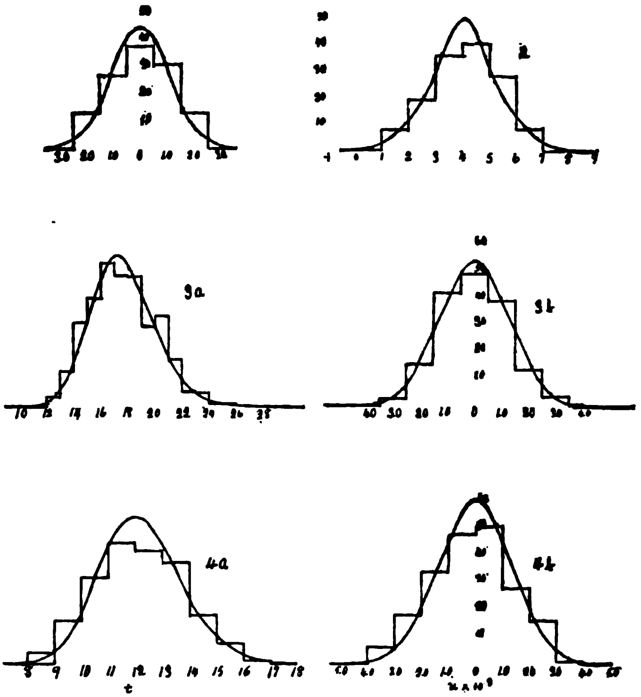

Fig. 1.

Table I.

Drop No. 1. Temperature = 23° C. *Pressure* = 2.12 *cm.*

t for .522 cm.		t' for .522 cm.		
40.6	39.4	14.1	13.9	V = .01311
40.5	38.6	13.9	14.2	V' = .03725
40.3	41.0	13.6	13.9	Volts = 334.5
39.0	39.0	14.0	14.0	h = 4.05×10^4
39.2	40.7	14.4	14.2	

$x\times .00746$ cm. for 10-second intervals.

+2.39	+1.50	+ .90	+.67	+.15	−.08	−.30	−.75	−1.12	−1.80
2.09	1.50	.90	.67	.15	.15	.30	.75	1.20	1.80
2.02	1.42	.10	.60	.08	.15	.37	.75	1.20	1.87
1.87	1.35	.90	.52	.08	.15	.37	.75	1.20	1.87
1.80	1.27	.90	.52	.08	.22	.37	.82	1.22	1.87
1.74	1.27	.82	.52	.00	.22	.37	.82	1.27	1.94
1.72	1.27	.82	.52	.00	.22	.45	.82	1.27	2.09
1.65	1.20	.75	.52	.00	.22	.45	.82	1.35	2.32
1.65	1.20	.75	.37	.00	.30	.52	.97	1.42	2.46
1.65	1.20	.75	.37	.00	.30	.60	.97	1.57	
1.65	1.05	.75	.37	.00	.30	.60	.97	1.57	
1.50	.97	.75	.30	.00	.30	.67	.97	1.67	
1.50	.90	.75	.15		.30	.67	.97	1.72	

obs $x_a = 8.95\times10^{-3}$ cm. cal $x_a = 8.76\times10^{-3}$.

$x_1\times .00746$	$x_2\times .00746$	cal n	obs n
+2.5	+1.5	9.6	13
+1.5	+0.5	29.7	31
+0.5	−0.5	43.4	38
−0.5	−1.5	29.6	27
−1.5	−2.5	9.6	13

§ 3. *Comparison of the observed and calculated values of the displacement produced in a fixed time when an outside force is acting upon the droplet.*

In this case the drop was allowed to move slowly against g and its displacement in successive 10-second intervals was taken. The results are tabulated in Table II. in a manner exactly like that used in the previous section, "cal n" being taken from (29) and u_a from (28). The graphical comparison is shown in curve 2, Fig. 1.

§ 4. *Comparison of the observed and calculated values of the time of fall through a fixed distance.*

Most of the data were taken by this method because it is capable of giving higher accuracy than that obtainable with either of the other

TABLE II.

Drop No. 2. Temperature = 21° C. Pressure = 2.08 cm.

t for .522 cm.		t'' for .522 cm.		
28.8	26.0	17.0	17.1	$V = .01933$
27.1	26.3	19.4	16.1	$V'' = .00303$
26.0	27.0	16.2		$V + V' = .01118$
27.5	27.6	17.5		Volts = 107.5
				$k = 5.91 \times 10^4$

$b + .00746$ for 10-second intervals.

1.4	2.5	3.0	3.4	3.8	4.2	4.5	5.0	5.2	5.7
1.5	2.5	3.1	3.4	3.8	4.2	4.5	5.0	5.2	5.9
1.5	2.5	3.1	3.4	4.0	4.2	4.5	5.0	5.3	5.9
1.7	2.6	3.1	3.5	4.0	4.3	4.6	5.0	5.3	6.1
1.8	2.7	3.1	3.5	4.0	4.3	4.6	5.0	5.3	6.2
1.9	2.8	3.2	3.6	4.0	4.3	4.6	5.0	5.4	6.2
1.9	2.8	3.2	3.6	4.0	4.3	4.6	5.1	5.4	6.2
2.0	2.8	3.2	3.6	4.0	4.4	4.7	5.1	5.4	6.3
2.1	2.9	3.2	3.7	4.1	4.4	4.7	5.2	5.4	6.4
2.1	3.0	3.2	3.7	4.2	4.5	4.7	5.2	5.5	
2.1	3.0	3.2	3.7	4.2	4.5	4.8	5.2	5.5	
2.2	3.0	3.3	3.7	4.2	4.5	4.9	5.2	5.5	
2.3	3.0	3.3	3.8	4.2	4.5	4.9	5.2	5.5	
2.5	3.0	3.3	3.8	4.2	4.5	5.0	5.2	5.5	

obs $u_a = 2.365 \times 10^{-3}$. cal $u_a = 2.32 \times 10^{-3}$.

$b_1 + .00746$	$b_2 + .00746$	cal n	obs n
$-\infty$	0	.00	0.0
0	1	.88	0.0
1	2	5.56	7.5
2	3	20.04	18.5
3	4	38.80	35.0
4	5	39.40	39.5
5	6	22.40	27.5
6	7	6.65	8.0
7	$+\infty$	1.32	0.0

methods. In all of the observations recorded in this section, except those relating to Drop No. 8, the variation in the time of fall was taken under the influence of gravity alone. But since (21) shows that V is proportional to $1/ak$ while u_a is proportional to $1/\sqrt{ak}$ the Brownian movements would affect the velocity less at a low pressure than at a high pressure. In order to work, however, at a low pressure where the Brownian movements are large, for Drop No. 8 the velocity was made small by superposing an electric field upon the gravitational field. However there is an objection to this procedure since a very slight change in the strength of the electrostatic field produces a very perceptible change in the velocity of the drop.

The results are tabulated in a manner similar to that used in sections 2 and 3. For example in Table III., Part I., in the column "t'" are given values of the time in seconds required for the singly charged drop to move .522 cm. under the influence of the electrostatic field; and similarly in the columns, t'', t''' and t^{iv} are given the values of the time for the same drop when it is charged with two, three and four elementary charges. It is seen from the values in the last column that

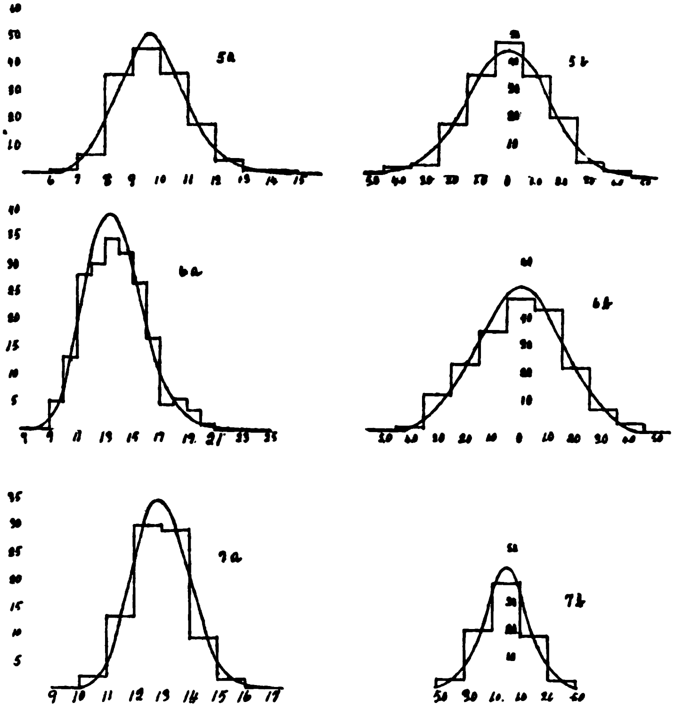

Fig. 2.

$$V+V' = \tfrac{1}{2}(V+V'') = \tfrac{1}{3}(V+V''') = \tfrac{1}{4}(V+V^{iv}),$$

as the theory predicts. Therefore the values $\frac{1}{2}(V+V'')$, $\frac{1}{3}(V+V''')$ and $\frac{1}{4}(V+V^{iv})$ were used to determine the mean value of $V+V'$. Also in the last column is given the value of h computed from (39). In part II. are given the successive times of fall through .0373 cm. At the bottom are given the average values obtained from these times of fall. V is computed by (33) and "cal u_a" by (40). The theory predicts that the average component of the displacement in one second along a line should be $.945\times10^{-3}$ and the displacement observed was $.990\times10^{-3}$. In Part III. is shown the comparison of the observed and calculated

TABLE III.

Drop No. 3. *Temperature* = 20° *C.* *Pressure* = 23.1 *cm.*

Part I. $b=.522$ cm. **Volts = 637.**

t'	t''	t'''	t^{iv}	
58.0	26.0	16.3	11.6	$V=.00213$
59.0	25.5	16.4		$V'=.00881$
58.2	25.7	17.0		$V''=.0205$
59.5	26.3	16.5		$V'''=.0315$
58.4	26.0			$V^{\text{iv}}=.0437$
	26.4			Mean $V+V'=.0111$
	25.9			$h=35.6\times10^4$
	26.3			

Part II. **Values of t.** $b=.0373$ cm.

12.2	14.6	15.6	16.3	17.0	17.5	18.3	19.0	20.0	21.4
12.4	14.6	15.6	16.3	17.0	17.5	18.3	19.0	20.0	21.5
12.5	14.6	15.6	16.3	17.0	17.6	18.3	19.0	20.0	21.4
13.0	14.7	15.7	16.4	17.0	17.6	18.4	19.0	20.1	21.5
13.2	14.8	15.7	16.4	17.0	17.6	18.4	19.0	20.1	21.6
13.4	14.8	15.7	16.4	17.0	17.6	18.4	19.1	20.2	21.7
13.6	14.8	15.7	16.4	17.0	17.7	18.4	19.2	20.2	21.7
13.7	14.8	15.7	16.4	17.0	17.7	18.4	19.2	20.2	21.8
13.8	14.8	15.7	16.4	17.0	17.7	18.4	19.2	20.3	22.0
13.8	14.8	15.8	16.5	17.0	17.7	18.5	19.4	20.3	22.2
13.8	14.9	15.8	16.5	17.0	17.8	18.5	19.4	20.4	22.2
13.9	14.9	15.8	16.5	17.1	17.8	18.5	19.4	20.4	22.5
14.0	14.9	15.8	16.6	17.1	17.8	18.5	19.4	20.4	22.5
14.0	15.0	15.8	16.6	17.1	17.8	18.5	19.4	20.4	22.6
14.0	15.0	16.0	16.6	17.1	17.8	18.6	19.4	20.4	23.2
14.0	15.0	16.0	16.6	17.1	17.8	18.6	19.4	20.4	23.3
14.0	15.0	16.0	16.7	17.2	17.8	18.6	19.5	20.4	23.3
14.0	15.1	16.0	16.7	17.2	17.8	18.6	19.5	20.4	23.3
14.0	15.1	16.0	16.7	17.2	18.0	18.6	19.5	20.4	23.3
14.0	15.2	16.0	16.7	17.2	18.0	18.6	19.5	20.4	24.3
14.0	15.2	16.0	16.7	17.2	18.0	18.6	19.5	20.4	25.4
14.1	15.3	16.1	16.7	17.2	18.0	18.7	19.6	20.6	26.3
14.2	15.3	16.2	16.7	17.3	18.0	18.7	19.6	20.6	20.9
14.2	15.3	16.2	16.7	17.3	18.0	18.7	19.6	20.6	21.0
14.3	15.4	16.2	16.7	17.4	18.0	18.8	19.7	20.6	21.0
14.3	15.4	16.2	16.8	17.4	18.0	18.8	19.8	20.7	21.1
14.4	15.4	16.2	16.8	17.4	18.1	18.8	19.8	20.7	21.3
14.4	15.5	16.2	16.8	17.4	16.1	18.8	19.9	20.7	21.3
14.5	15.5	16.3	16.8	17.4	18.1	18.8	19.9	20.7	
14.5	15.5	16.3	16 8	17.4	18.1	18.8	19.9	20.8	
14.5	15.5	16.3	16.9	17.5	18.2	18.8	20.0	20.8	
14.6	15.6	16.3	16.9	17.5	18.2	18.8	20.0	20.8	

$t_a=17.65$, $V_a=.00211$, $V=.00213$, $\eta=321$, obs $u_a=.990\times10^{-3}$, cal $u_a=.945\times10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	12	0.0	.69	$+\infty$	$+3.5$	0	.5
12	13	3.5	3.3	$+3.5$	$+2.5$	5	5.3
13	14	13.0	10.9	$+2.5$	$+1.5$	31	27.1
14	15	31.0	24.2	$+1.5$	$+0.5$	74	75.3
15	16	35.0	40.8	$+0.5$	-0.5	98	105.0
16	17	53.0	52.4	-0.5	-1.5	78	75.3
17	18	48.5	54.7	-1.5	-2.5	27	27.1
18	19	48.0	47.7	-2.5	-3.5	7	5.3
19	20	29.5	35.6	-3.5	$-\infty$	1	.5
20	21	33.5	23.5				
21	22	12.5	13.7				
22	23	5.5	7.3				
23	24	5.0	3.6				
24	25	1.0	1.6				
25	26	1.0	.69				
26	∞	1.0	.47				

Table IV.

Drop No. 4. Temperature $=21°$ *C. Pressure* $=14.3$ *cm.*

Part I.			$b=.522$ cm.				Volts $=483.5$.
t			t'		t''	t'''	
							$V=.00307$
160	166	182.8	73.5	68.7	29.7	18.4	$V'=.00742$
158	187	175.2	71.0	70.2	28.5	18.9	$V''=.01754$
158.9	178	164.4	72.8	67.4	29.1	18.8	$V'''=.0279$
167.0	175.6	178.0	71.0		29.0	t^{iv}	$V^{\text{iv}}=.0387$
161.5	176.4	169.2	68.0			13.5	$V^{\text{v}}=.0607$
166.2	168.0		70.0			t^{iv}	Mean $V+V'=.01041$
170.0	170.0		70.4			8.6	$h=28\times10^4$

$t_a=12.12$, $V_a=.00308$, $V=.00310$, $\eta=202$, obs $u_a=1.061\times10^{-8}$, cal $u_a=1.057\times10^{-8}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	8	0	0	$+\infty$	$+4.0$	0	.24
8	9	4.0	1.4	$+4.0$	$+3.0$	6	2.1
9	10	16.0	10.5	$+3.0$	$+2.0$	18	11.8
10	11	32.0	31.4	$+2.0$	$+1.0$	34	32.2
11	12	44.5	50.7	$+1.0$	0.0	48	55.5
12	13	42.0	50.7	0.0	-1.0	51	55.5
13	14	37.5	33.9	-1.0	-2.0	28	32.2
14	15	18.0	16.2	-2.0	-3.0	16	11.8
15	16	7.5	6.3	-3.0	-4.0	1	2.1
16	17	1.0	1.6	-4.0	$-\infty$	0	.24
17	18	.5	.1				

distributions of the values of *t* and *u*. Curves 3*a* and 3*b*, which are plotted as explained in section 2, show graphically this same comparison. In all of the following tables the drop no. and the curve no. correspond. Table III. is complete, but in Tables IV.–IX. the observed values of *t* in Part II. have been omitted.

TABLE V.

Drop No. 5. *Temperature* = 20° *C.* *Pressure* = 9.97 *cm.*

Part I.			**b = .522 cm.**				**Volts = 318.**
t			t'	t''	t'''	t^{iv}	
127.2	132.2	135.5	107.8	38.0	22.7	17.8	$V=.003911$
129.7	132.2	136.1	106.1	38.2	23.2	17.0	$V'=.004790$
129.9	132.3	136.4	108.0	38.5	23.2	17.2	$V''=.01352$
130.2	132.4	137.8	106.5	38.3	24.1	17.1	$V'''=.02222$
130.8	133.2	138.4	109.0	38.4	23.8	t^{v}	$V^{iv}=.03022$
131.4	133.7	138.8	113.0	39.4	23.9		$V^{v}=.03880$
131.4	134.2	139.5	113.0	39.6		13.3	Weighted mean $V+V'$
132.2	134.7		108.8			13.8	$=.0869$
							$h=22.7\times10^4$

$t_a=9.72$, $V_a=.00383$, $V=.00388$, $\eta=171$, obs $u_a=1.162\times10^{-8}$, cal $u_a=1.183\times10^{-8}$.

Part III. Distribution of t.				**Distribution of u.**			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	7	1.	.7	$+\infty$	+3.5	2	1.6
7	8	6.5	10.5	+3.5	+2.5	3	6.3
8	9	35.5	30.7	+2.5	+1.5	18	18.2
9	10	45.0	48.2	+1.5	+0.5	36	37.3
10	11	36.0	36.0	+0.5	−0.5	48	44.2
11	12	17.5	16.0	−0.5	−1.5	36	37.3
12	13	4.5	4.6	−1.5	−2.5	21	18.2
13	14	1.0	1.1	−2.5	−3.5	5	6.3
14	∞	1.0	0.2	−3.5	$-\infty$	2	1.6

TABLE VI.

Drop No. 6. *Temperature* = 20° *C.* *Pressure* = 7.0 *cm.*

Part I.			**b, = .521 cm.**	**Volts = 828.**	
t	t'		t''		
The value of V is obtained from data in Part II.	24.5	25.0	11.2	$V=.00277$	
	24.6	24.7	11.5	$V'=.0210$	$h=21.7\times10^4$
	24.6	24.6	11.7	$V''=.0446$	
	24.3	25.6	11.9		
	24.7	25.2	12.0	Weighted mean $V+V'=.02373$	
	24.6	24.6			

$t_a=13.78$, $V_a=.00274$, $V=.00277$, $\eta=200$, obs $u_a=1.256\times10^{-8}$, cal $u_a=1.215\times10^{-8}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	$u_1\times10^3$	$u_2\times10^3$	obs n	cal n
0	9	0	0.3	$+\infty$	+3.5	1	2.1
9	10	5	1.8	+3.5	+2.5	13	7.8
10	11	13	6.8	+2.5	+1.5	24	22.3
11	12	28	16.7	+1.5	+0.5	36	42.0
12	13	30	28.1	+0.5	−0.5	48	51.6
13	14	34.5	35.3	−0.5	−1.5	44	42.0
14	15	32.0	25.0	−1.5	−2.5	23	22.3
15	16	26.5	28.9	−2.5	−3.5	8	7.8
16	17	16.5	20.5	−3.5	$-\infty$	3	2.1
17	18	4.5	13.8				
18	19	5.5	7.2				
19	20	3.5	3.6				
20	21	1.5	1.7				
21	22	0.5	0.8				
22	∞	0.0	0.5				

Table VII.

Drop No. 7. Temperature = 20° C. Pressure = 6.5 cm.

Part I.			$b = .521$.		Volts = 668.
t	t'		t''	t	
Value of V is obtained from data in Part II.	33.7	35.6	14.2		$V = .00579$.
	33.0	34.7	14.4	9.1	$V' = .01417$.
	32.8	33.0	14.7	9.3	$V'' = .0355$.
	34.4	35.4			$V''' = .0566$.
	35.8	34.0		t	$V^{iv} = .0755$.
	34.9				$k = 20.2\times10^4$
				6.9	Weighted mean $V + V' = .02024$.

$t_a = 12.89$, $V_a = .00577$, $V = .00579$, $\eta = 84$, obs $u_a = 1.278\times10^{-8}$, cal $u_a = 1.252\times10^{-8}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	10	0.0	0.04	$+\infty$	+5	0	.06
10	11	2.0	1.6	+5	+3	3	2.3
11	12	13.0	13.2	+3	+1	21	19.7
12	13	29.5	31.2	+1	−1	38	40.0
13	14	28.5	26.5	−1	−3	19	19.7
14	15	9.0	9.5	−3	−5	3	2.3
15	16	2.0	1.7	−5	$-\infty$	0	.06
16	∞	0.0	0.2				

Particular attention is to be called to Drop No. 8 which showed variations in the time of fall from 2 seconds to 25 seconds, the average velocity being 10 per cent. lower than the actual velocity due to the constant outside force. In this rather extreme case the observed and calculated values show a very good agreement.

TABLE VIII.

Drop No. 8. *Temperature* = 20° *C.* *Pressure* = 2.98 *cm.*

Part I.		b = .522 cm.		**Volts = 162.7.**
t		t''	t'''	
43.5	49.0	32.5	17.5	V = .01112
47.5	49.8	32.0	18.0	V'' = .01592
43.4	49.0	32.6	18.5	V''' = .02888
45.1	45.0	33.2	18.0	Mean $V + V'$ = .01346
45.1	47.6	33.2	18.4	$h = 7.52 \times 10^4$
47.4	47.2	33.4		
47.4	48.6	33.4		
47.4	48.4			

$t_a = 7.29$, $V_a' = .00205$, $V' = .00226$, $\eta = 411$, obs $u_a = 1.95 \times 10^{-8}$, cal $u_a = 2.05 \times 10^{-8}$.

Part III. Distribution of t'.				**Distribution of u.**			
t_1'	t_2'	obs n	cal n	u_1	u_2	obs n	cal n
0	2	.5	0.9	+8	+6	2	3.7
2	3	9.0	13.4	+6	+4	17	20.5
3	4	35.0	38.1	+4	+2	70	65.2
4	5	57.5	57.7	+2	0	108	115.2
5	6	55.5	60.8	0	−2	113	115.2
6	7	60.5	56.1	−2	−4	53	65.2
7	8	50.5	47.5	−4	−6	18	20.5
8	9	50.0	36.8	−6	−8	5	3.7
9	10	26.0	28.4				
10	11	15.5	21.3				
11	12	17.0	14.4				
12	13	12.5	10.7				
13	14	8.5	7.5				
14	15	4.0	5.5				
15	20	6.5	9.4				
20	∞	2.0	2.1				

TABLE IX.

Drop No. 9. *Temperature* = 20° *C.* *Pressure* = 2.28 *cm.*

	Part I.		b = .521 cm.		**Volts = 353.**
t	t'		t''	t	
The value of V is obtained from data in Part II.	16.8	17.8	8.0	5.4	V = .00805
	16.8	18.4	7.9	5.0	V' = .03024
	17.0	17.6	8.0	4.8	V'' = .0657
	16.8	17.0	7.8	4.8	V''' = .1042
	16.6				$h = 409 \times 10^4$
					Weighted mean $V + V'$ = .0378

$t_a = 9.35$, $V_a = .00795$, $V = .00805$, $\eta = 85$, obs $u_a = 2.43 \times 10^{-8}$, cal $u_a = 2.38 \times 10^{-8}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	6	0	0	$+\infty$	+8	0	.9
6	7	1	.8	+8	+6	1	2.6
7	8	9	8.4	+6	+4	8	7.0
8	9	27	24.0	+4	+2	9	13.3
9	10	25	27.8	+2	0	27	18.5
10	11	16	16.8	0	−2	19	18.5
11	12	4	5.7	−2	−4	10	13.3
12	13	3	1.4	−4	−6	8	7.0
13	∞	0	0.2	−6	−8	3	2.6
				−8	$-\infty$	0	.9

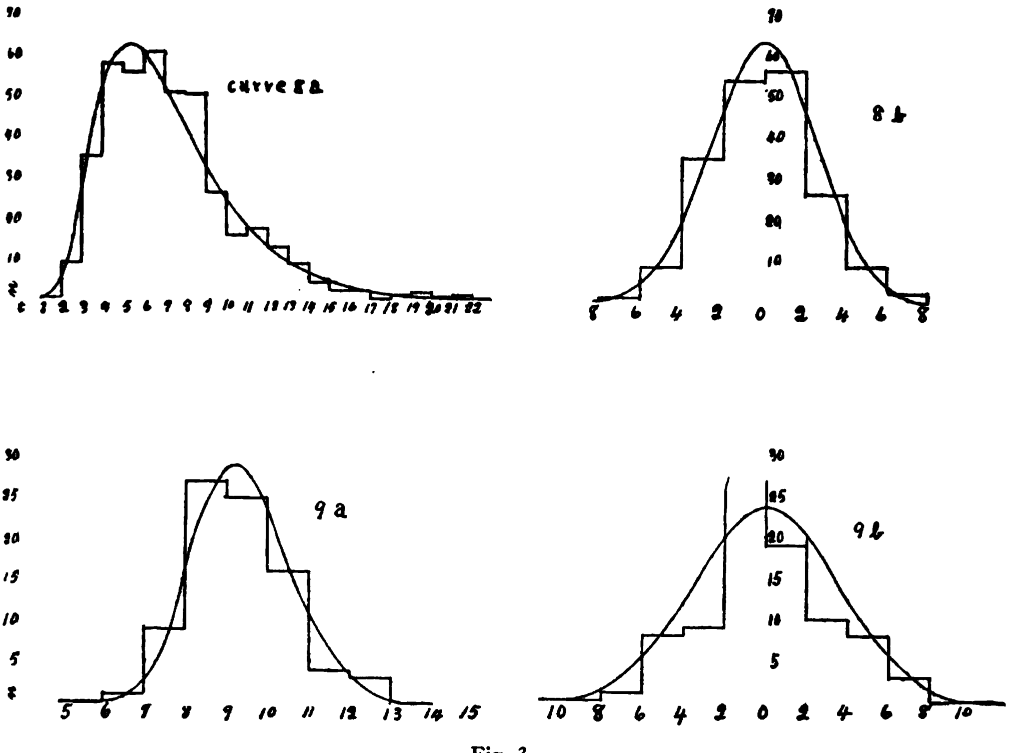

Fig. 3.

Before the condenser plates were put into the large brass cylinder described above, 341 observations were taken upon a single oil drop. 151 values of t were taken for b = .00744 cm.; 155 values for $b = 2\times$ .00744 cm.; and 34 values for $b=5\times.00744$ cm. The comparison of the observed and calculated distributions for these three cases is shown in curves 10a, 10b, and 10c. The observed values of u_a were $.792\times10^{-8}$, $.846\times10^{-8}$ and $.725\times10^{-8}$. The comparison of the observed and calculated 341 values of *u* is shown in Curve 11. The two broken curves represent two different groupings of the same values of *u*.

Since for oil drops suspended in air at atmospheric pressure the formula

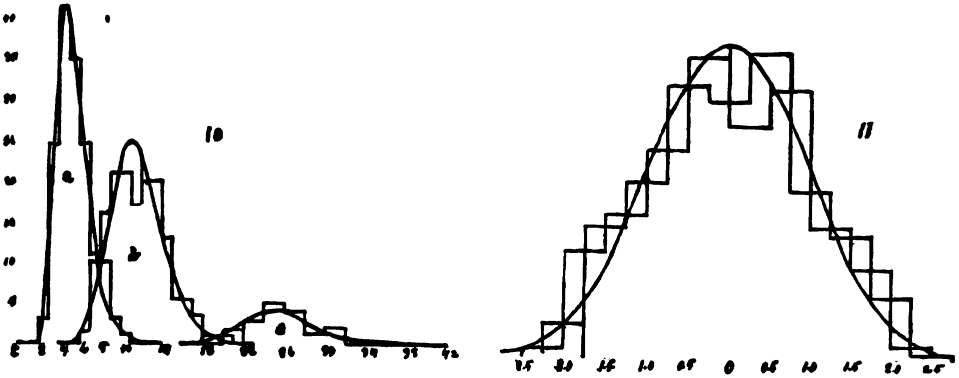

Fig. 4.

$$V=\frac{2}{9}\frac{ga^2(\sigma-e)}{\mu}\left\{1+.817\frac{l}{a}\right\}$$

has been shown to hold it was used to determine *a* and *k* with the result that

$$a=31.9\times10^{-6} \quad \text{and} \quad k=.810.$$

Substituting these values in (27) we get

$$\epsilon=6.40\times10^{-14}$$

and since

$$e=\frac{3}{2}\frac{RT}{N},$$

we get ($G=296$ and $R=82.9\times10^{6}$)

$$N=57.5\times10^{22}.$$

We see thus that the Brownian movement theory developed in Part I. accounts completely for the variation in the observed displacements and times of fall, and gives a fairly accurate means of determining molecular magnitudes.

§ 5. *Determination of the value of Ne for gaseous ionization.*

Townsend's and Frank and Westfall's work[1] on mobility and diffusion coefficients is the only evidence, so far, that has justified the assumption that the value of *Ne* for gaseous ionization is the same as in electrolysis.

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[1] For a discussion of their results see Millikan and Fletcher, Phil. Mag., June, 1910.

The fact that the theoretical and observed distributions and the average absolute values of the displacement agree, shows that this assumption is correct. To show how close is this agreement (40) is solved for $\sqrt{Ne}$. The resulting value for each drop is given in Table X.

TABLE X.

Drop No.	$u_a \times 10^3$	T	$V+V'$	Volts.	$\sqrt{Ne}\times 10^{-7}$	η
1	2.83	294	.05036	334.5	1.68	125
2	2.365	294	.01118	107.5	1.67	136
3	.990	293	.1110	637	1.645	321
4	1.061	294	.01041	483.5	1.695	202
5	1.162	293	.00868	318	1.73	171
6	1.256	293	.0237	828	1.65	200
7	1.278	293	.0201	668	1.66	84
8	1.950	293	.133	162.7	1.785	411
9	2.43	293	.0380	353	1.65	85

If weights be assigned according to the number of observations taken as shown in the last column of the above table, there results for *the weighted mean value which represents an average of 1,735 values of u*

$$\sqrt{Ne} = 1.698 \times 10^7$$

or

$$Ne = 2.88 \times 10^{14}.$$

The value of Ne obtained by depositing silver by an electric current, when expressed in electrostatic units is 2.896×10^{14}.

If now the value of N obtained in section 4 is substituted in the above value of Ne we get[1]

$$e = 5.01 \times 10^{-10},$$

which is within 2 per cent. of the value obtained by Millikan. It is to be noticed that *both N and Ne and consequently e are determined by the above method from the same set of experiments and not from totally different types of experiments as heretofore has always been the case, and further that these experiments furnish a direct proof that the value of the elementary charge on the oil drop which it received by catching an ion from the air is the same as the charge on the silver ion in electrolysis.*

§ 6. *Application of the theory to Ehrenhaft's*[2] *and Przibram's*[3] *work on the value of e.*

---

[1] This shows there is no longer any discrepancy in the values of e obtained by the Millikan method and the Brownian movements method as had appeared to be the case from Perrin's observations on Brownian movements in liquids.

[2] Wien. Ber., 119, 2a, March, 1910.

[3] Wien. Ber., 119, 2a, June, 1910.

In a preliminary report of this work which was published in the Phys. Zeit., VII., 1911, I computed the distribution of the values of t and t' treating the data in Table V. of Ehrenhaft's work as if it were taken all upon one particle. Using Cunningham's formula and assuming the density of the particles to be that of metallic platinum, as Ehrenhaft supposed it to be h was calculated from (26) and found to be given by

$$h = 4.55 \times 10^4.$$[1]

When, however, h is computed from (39), $V+V'$ being computed the values $t_a=6.86$ and $t_a'=4.18$, we have

$$h=23.6\times 10^4.$$

This very great discrepancy can, in my judgment, be explained only by assuming that the density of the particles which he observed was not the density of the metallic platinum. For other reasons Regener[2] has come just recently to the same conclusion.

Using this last value of h we get from (26)

$$ak = 11.44 \times 10^{-6},$$

and from (19)

$$a = 16.56 \times 10^{-6},$$

and from (20)

$$\sigma = 3.3.$$

From this it appears that the density of the platinum particles which Ehrenhaft observed was 3.3 instead of 21.5. The correctness of this statement can be checked if 100 or more observations can be taken upon a single particle. The only data available at present is that taken upon different particles. In curves 12 and 13 (Fig. 5) is shown the comparison between the calculated and observed distribution of t and t'. The smooth curve is the theoretical distribution of the times of fall for a single particle having the average size of those recorded in Ehrenhaft's Table V., while the broken curve gives the observed distribution as taken from this same table. As we would expect there is no such agreement as when the observations are all taken upon the same particle, but the theoretical variation of the values of t and t' is amply sufficient to explain all of Ehrenhaft's irregular values of e. It also indicates that the low value of e is probably due to an error in the density, but this can not be shown conclusively until more observations are taken upon a single particle.

To show the relation of Przibram's work to the present theory a somewhat different treatment may be used because he obtained two[1] values of t and t' for the same particle. A calculation of the times of fall shows that the variation is not as large as that shown in his tables which only means that the particles were of different sizes. But an idea of the differences in two successive times of fall may be obtained by computing the variation for his average-sized particle.

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[1] Due to some minor corrections this value does not agree exactly with the value given in the preliminary report.

[2] Phys. Zeit., XI., 1911.

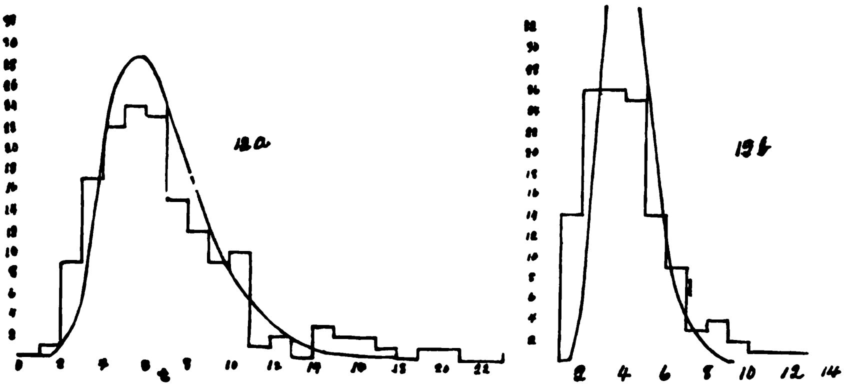

Fig. 5.

For 220 observations taken upon "Phosphornebel" (Table V. of his work) the average time of fall through .0416 cm. is 15.2 seconds. Then

$$V = .00275, \quad a = 44.4 \times 10^6 \text{ cm.}, \quad k = .85, \quad h = 78 \times 10^4,$$

which gives for the probability that a time of fall will be between t_1 and t_2 the equation

$$P = 1.374 \int_{t_1}^{t_2} \frac{t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}}}{2} \cdot e^{-\frac{78}{t}(4.15-.275t)^2} dt.$$

The following values of P were calculated by this formula:

TABLE XI.

t_1	t_2	P
12	13	0.024
13	14	0.13
14	15	0.31
15	16	0.32
16	17	0.17
17	18	0.04
18	19	0.004

---

[1] Recently both Ehrenhaft and Przibram have taken several observations on a single particle but the number is still too small to make it possible to apply stat stical formulæ.

The probability that any two times occur successively is the product of the probabilities that they will occur separately. For example, the probability that a time between 14 and 15 is followed by a time between 16 and 17 is .31 × .17 = .053. When such a combination occurs the per cent. of difference lies between 14 and 21. Out of 110 double observations 5 or 6 should show a difference of 14 per cent. to 21 per cent. due to the above combinations. Taking all possible combinations the following are obtained:

Between	0	per	cent.	and	7	per	cent.	about	45	observations.
"	7	"	"	"	14	"	"	"	37	"
"	14	"	"	"	21	"	"	"	20	"
Above	21	"	"					"	10	"

By calculating the per cent. of difference in two successive times of fall from Przibram's Table V. we have

Between	0	per	cent.	and	7	per	cent.	55	observations.
"	7	"	"	"	14	"	"	26	"
"	14	"	"	"	21	"	"	16	"
Above	21	"	"					13	"

The agreement is sufficiently good to show that by the Brownian movement theory we can account for the differences which he obtained. Also these differences are sufficient to show why he obtained an overlapping of the values of 1*e* and 2*e* or 2*e* and 3*e*, etc.

CONCLUSION.

It has been shown that:

1. The continual agitation of a small particle suspended in a gas, known as Brownian movements is entirely explained by the kinetic theory of gases, both qualitatively and quantitatively.

2. The value of *Ne* obtained from gaseous ionization is the same as that obtained from electrolysis.

3. The irregular values of *e* apparently resulting from the work of Ehrenhaft and Przibram are entirely explained by the Brownian movement theory.

For this work I am much indebted to Professor R. A. Millikan, who has worked with me while all of the above data were taken, and under whose personal direction this research has been done, and also to Professor A. C. Lunn for his aid and helpful criticism on the first part of this work.

RYERSON PHYSICAL LABORATORY,
April 25, 1911.

THE RADIANT EFFICIENCY OF ARC LAMPS.

By Henry Phelps Gage.

THE object of the present investigation was to determine the radiant efficiency and the mechanical equivalent of the light from the right angle carbon arc and the Bremer flaming arcs.

The symbols used in this paper are:

R = total watts radiated.
L = light energy; watts of radiant energy of wave-lengths visible to the eye.
W = radiant energy of wave-lengths to which water is transparent.

The ratios here determined are called:

L/R = radiant efficiency.
W/R = "water-bath" efficiency.

Discussion of the Limits of Visibility.

When determining radiant efficiency by an integration method such as that of Langley[1] or of Ångström,[2] certain arbitrary limits are chosen to divide the visible from the invisible parts of the spectrum. These methods are based on the following definition of radiant efficiency.

$$\text{Eff.} = \frac{L}{R} = \frac{\int_{\lambda_1}^{\lambda_2} I d\lambda}{\int_0^{\infty} I d\lambda} = \frac{\text{energy visible part of spectrum}}{\text{total energy radiated}},$$

where I is the intensity of the light and λ_2 and λ_1 are the upper and lower limits of visibility respectively. For most light sources the energy in the ultra-violet is so small that the lower limit λ_1 can be taken as zero with no appreciable error, the energy of the infra-red is however so great that a slight change in the position of the limit in the red causes a great change in the value of L.

Langley,[3] the first to use the integration method, chose the limit .70μ.

Later workers moved the limit of integration far beyond this point to the A line, .76μ.

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[1] Science, June 1, 1883.

[2] Phys. Rev., 17, 302, 1903.

[3] Phil. Mag., 30, 260, 1890.

P. G. Nutting[1] criticizes this as being too far from the natural physiological limit, but suggests no other.

While the human eye will respond to radiation of wave-length $.76\mu$ and under favorable conditions to even as great wave-lengths as $.82\mu$,[2] this response is very slight. Hence it was thought advisable to choose a new limit which, while arbitrary, would correspond reasonably well with the physiological limit of the human eye.

The principle adopted was that the limit should be so chosen that all light beyond the limiting wave-length should be so small as to be negligible in comparison with the total light.

König and Brodhun[3] have shown that if a white surface is illuminated by two patches of light side by side whose intensities differ by 1.6 per cent. the difference can only just be detected. Therefore in choosing the limit it would appear that the rejected light may be as great but should not be greater than 1.6 per cent. of the total.

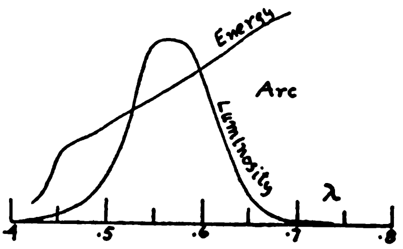

Fig. 1.
Luminosity curve from Abney and Festing.

In the spectrum of the positive crater of the carbon arc, for example, there is almost no visible light beyond $.70\mu$, but in this region the energy is very intense. The result is that changing the limit from $.70\mu$ to $.76\mu$ increases the energy enormously while hardly changing the visual effect at all; conversely, moving the limit from $.76\mu$ to $.68\mu$ results in a decrease in energy out of all proportion to the decrease in light.

The choice of a new limit was made by integrating luminosity curves. The total area of such a curve was taken as the total luminosity and the area beyond different wave-lengths was measured with a planimeter. The ratio of the small area beyond the given wave-length to the total area would be the amount of light lost if all radiation of greater wave-length were removed. Such measurements were made on a luminosity curve of Abney and Festing[4] (Fig. 1), on the red sensation curve of König[5] and on some curves of my own. The results expressed in curve form (Fig. 2) indicate the percentage of the total light lost if the red end of the spectrum were removed to the given wave-length.

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[1] Electrical World, Vol. 51, p. 1371.

[2] The strong infra-red line of the sodium arc, see Becquerel, Comptes Rendus, Vol. 97, p. 73.

[3] Sitzungsberichte der Königlichen Baierische Academie der Wissenschaft, Berlin, pp. 917–931, 1888, II. Also table in Bulletin of the Bureau of Standards, Vol. 5, p. 286.

[4] Phil. Trans., 177, 423, 1886.

[5] Zeit. Psy. Phys. des Sinnesorgane, 4, 312, 1893. Also Gesammelte Abhandlung, p 286.

From these data and from the general appearance of the spectrum it was decided to use as the limit in the red .68μ. The curves show that with this limit the light removed is less than 1.6 per cent. of the total.

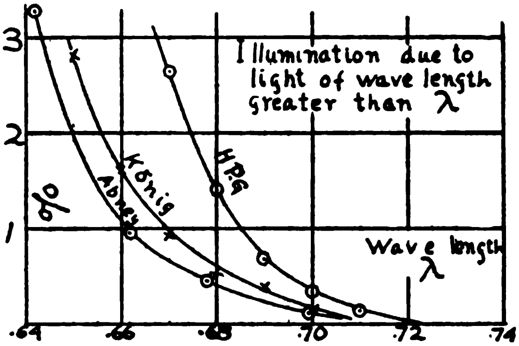

Fig. 2.

The limit is easily located in the arc spectrum of a mixture of lithium and potassium, being nearly half way between the lithium line .671μ and the potassium doublet .691μ. Also the absorption spectrum of neodymium shows a dark line at .68μ.

The limit in the violet could be determined in the same way but is of no great importance, as the energy of the ultra-violet part of the spectrum with most sources is so small that it can safely be neglected. In the study of the arc however it seemed advisable to arrange the apparatus to remove all radiation less than .4μ, thus allowing the cyanogen band of the carbon arc at .42μ to pass but excluding that at .388μ. Between these two bands there is practically no light.

APPARATUS.

In the work to be described a modification of the method of Ångström was used. The apparatus was similar to his, the main difference being

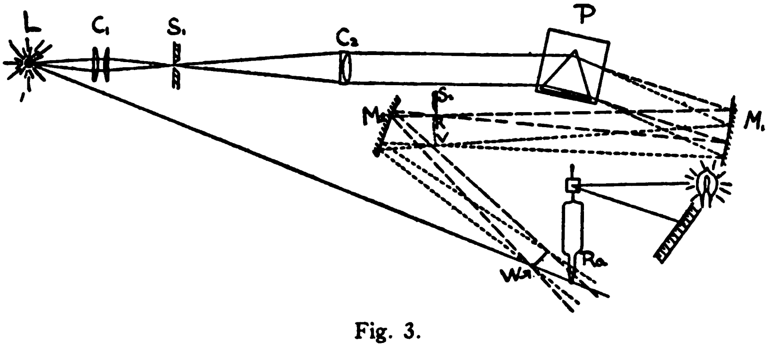

Fig. 3.
Arrangement of apparatus to measure L'/R.

that Ångström used two separate sources of light, one being dispersed into a spectrum, the energy of the other being measured direct; while in the present apparatus both the direct and the modified light come from the same source.

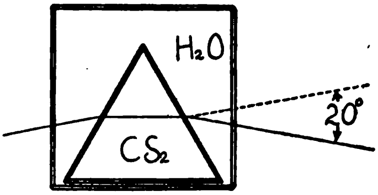

Fig. 4.
Compound prism.

Energy from the source *L* (Fig. 3) can reach the thermo-junction of the radiomicrometer *Ra* by either of two paths, (*a*) direct, no absorption except by air, (*b*) through the prism train *P*.

Light from the source is focused by the condenser C_1 on the adjustable slit S_1, is rendered parallel by the lens C_2, dispersed by the prism *P* and focused as a spectrum at *R*–*V* by the mirror M_1. The screen S_2 is placed in the red end of the spectrum so that it cuts off all of the infra-red to .68μ. The mirror M_2 reassembles the spectrum to a patch of white light at the radiomicrometer.

The intensity of the patch of direct light is fixed by the brightness and distance of the source *L*, but that of the other patch *W* can be varied by widening or narrowing the slit S_1 until it is of the same brightness as the direct light.

The prism consists in a 60° hollow prism of carbon bisulfide immersed in a square glass cell filled with distilled water. It gives a good dispersion with a deviation of but 20° from a straight line (Fig. 4).

The lenses are of glass.

The mirrors are plano-concave lenses, silvered on the concave side. The focal length of M_1 is 50 cm. and of M_2 is 25 cm.

THE RADIOMICROMETER (Fig. 5).

The suspension of the radiomicrometer was of no. 36 copper wire free from iron, to the bottom of which was soldered a small thermo-junction of bismuth and antimony. To the top of the loop was fastened a piece of silvered cover glass and the whole was suspended by a quartz fiber.

The radiomicrometer was provided with two windows. The one which faced the light had no glass in it in order not to absorb any energy, the one which faced the other way was so placed that the light source could be seen through the instrument. This window was covered with a plane glass.

The junction (Fig. 6) was made by cementing a rod of bismuth and one of antimony to a piece of mica with sealing wax and making connection between them at one end with fusible metal. The free ends were soldered to the copper loop with fusible metal and the junction dipped into dead black japalac. To get the small rods or wires of bismuth and antimony the metal was melted in a glass tube and the tube drawn down to capillary size. When cold this left the bore of the tube filled with a fine rod of the brittle metal. The ends of the metal were tinned with ordinary solder and then with Woods' fusible metal. It was then an easy matter to solder these rods which were left within the glass together and to the tinned ends of the copper loop.

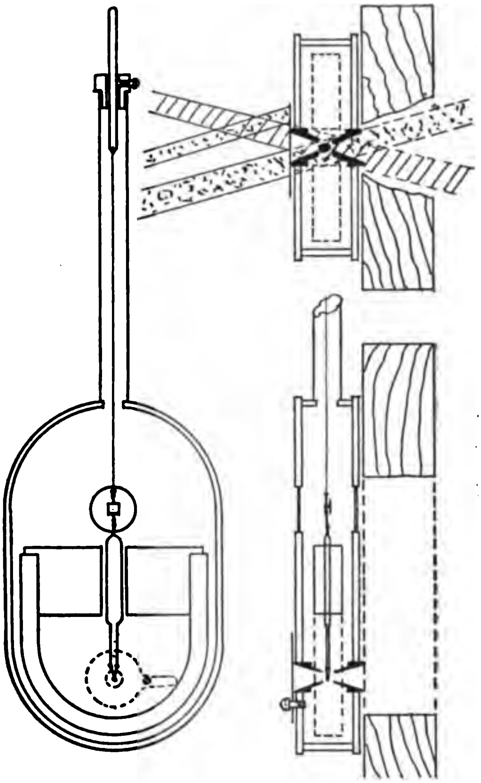

Fig. 5.
The radiomicrometer.

CALIBRATION.

The radiomicrometer used in this work did not need to be very sensitive as the energy to be measured was comparatively large. The ballistic method was used: the farthest point reached on the first swing being recorded in all cases.

To determine whether there was selective absorption by the black japalac surface of the junction, the ratio of W/R was determined for the positive crater of the carbon arc using a Sullivan galvanometer and a lecture room thermopile whose surfaces were covered with different substances: (1) camphor soot, (2) black japalac, (3) dull yellow shellac. The value of W/R came out nearly the same in all cases showing the proportion of energy absorbed to be nearly the same in the visible as in the invisible parts of the spectrum.

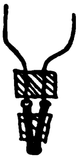

Fig. 6.
Radiomicrometer junction.

The scale of the radiomicrometer was calibrated by an acetylene flame moved to different distances. This showed that the "kick" and the steady deflection were proportional to the incident energy. Merritt has shown that the ballistic throw is proportional to the steady deflection both by experiment[1] and by theory.[2]

The radiomicrometer was also calibrated roughly in absolute units by a Hefner lamp and by a Nernst glower. The radiation of the Hefner lamp was taken from Ångström[3] as 11.3 watts.

Example:

Distance Hefner.	Kick.	Kick × d^2.	For 1 Watt: Kick × d^2.
35 cm.	7.42	9,100	808
50	3.75	9,400	832
			820

This value was checked by a Nernst lamp.

Input filament. 100 volts, 1.07 amps. = 107 watts; Radiation, mean spherical, 107 watts; Equatorial, 136 watts $\left(\frac{4}{\pi} \text{ times mean sph.}\right)$; Distance 100 cm.; Kick 12.5; $\frac{\text{kick} \times d^2}{136} = 920$. This is in general argeement with that obtained with the Hefner but is slightly greater as might be expected owing to the reflection from the heater just back of the glower.

In a similar way the more sensitive suspension no. 2 was found to have a constant of 3,540.

SOURCES.

The Right Angle Carbon Arc.—A simple hand feed arc lamp was used, either carbon of which could be moved separately. The carbons were held in the position shown in Fig. 7. The current was kept constant by feeding the carbons forward whenever the current showed signs of dropping. Soft-cored "Columbia Projector" carbons were used.

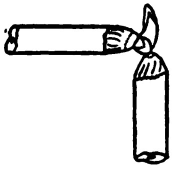

Fig. 7.
Right angle arc.

Tests were made using alternating and direct current. With the latter both the positive and negative craters were tried.

In some cases the lower carbon was shaded from the radiomicrometer so only the upper carbon could be seen. This was especially necessary when making measurements on the negative crater. The energy from the cyanogen arc between the electrodes was measured by shading both carbon tips. Both the light and energy from the arc is negligible in comparison with that from the hot tips.

With alternating current an inductor (choke coil) was used instead of a resistor because it furnished a much steadier current.

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[1] American Journal of Science, 37, 167, 1889.

[2] American Journal of Science, 41, 422, 1891.

[3] *L. c.*

The Bremer Flaming Arcs.—A lamp was kindly furnished by the late C. J. Toerring. It was made for alternating current and burns 8-mm carbons. An economizer and set of blow magnets caused the arc to take the position shown in Fig. 8. The electrodes used were 8-mm. "Excello" carbons known as "yellow" and "brilliant white."

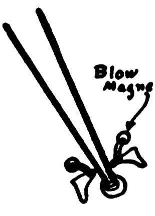

Fig. 8.
Flame arc.

METHOD.

Photometric Match.—The apparatus was so arranged that light from the source could strike the radiomicrometer after having traversed either of two paths, *i. e.*, either straight or through the prism train.

In front of the suspension was an aluminum shutter covered with a piece of white paper. By using screens with suitable holes the direct light was made to fall at the sides of the reassembled light (Fig. 9). The brightness of the reassembled light could be varied by opening or closing the slit S_1 until it was photometrically equal to the direct light. In making a photometric match the screen was viewed either through a red or a green glass. This was necessary on account of the great brightness of the patches and on account of the slight yellowish color of the mirrors which rendered a photometric match difficult. The energy of the spectrum being greater in the red than in the blue, the match was made through a red glass rather than through a blue glass.

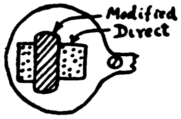

Fig. 9.
White shutter used as photometer.

This method gives visual equality at the shutter. The thermo-junction, however, is some distance behind the shutter necessitating a correction.

Call the light falling on the shutter L and R, that striking the thermo-junction L' and R'. The radiomicrometer will then give the ratio of L'/R', not L/R.

$R/R' = D'^2/D^2$, where D is the distance from the source to the shutter and D' that to the junction.

The value of L/L' is obtained by this reasoning:

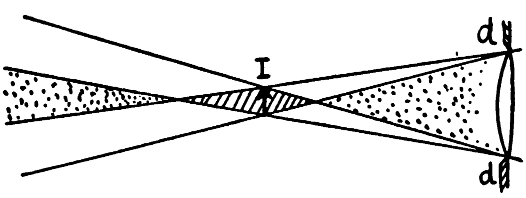

Fig. 10.
Image formation of an extended source.

Suppose I (Fig. 10) to be the image of an extended source of light of uniform brightness with sharply defined edges and d to be a diaphragm. If the radiomicrometer be placed at I or in the shaded area in the neighborhood of I it will receive light from the entire area of the diaphragm. An eye placed at this point will see the entire opening of the diaphragm lighted with the intrinsic brilliancy of the image I of the source. In this case as far as illumination is concerned the behavior is just the same as though there were an extended source of light at the diaphragm with the intrinsic brilliancy of I. Within the shaded area the energy will follow the inverse square law the distance being measured from the *diaphragm*. Outside the shaded area but within the dotted area the energy will follow the inverse square law but the distance must be measured from the *image* I, for now the radiomicrometer will receive light which has either passed through all parts of I or which would pass through all parts of I just as it would if I were the original source.

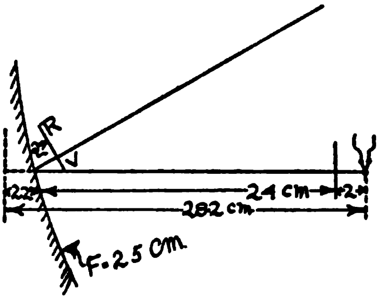

Fig. 11.
Position of diaphragm (R–V) for correcting L'/R.

In the case of the experiment the radiomicrometer was placed in the shaded area (light struck it from all parts of the diaphragm) and the position of the diaphragm was at the focus of the spectrum where the cut off screen was located. The *apparent* distance of the diaphragm was used.

Apparent distance of diaphragm (R–V, Fig. 11) to mirror	2.2 cm.

$$\frac{1}{2}-\frac{1}{25}=\frac{1}{2.2}$$

Apparent distance of diaphragm to screen	26.2 cm.
Apparent distance of diaphragm to junction	28.2 cm.

$$\text{Ratio } \frac{L}{L'}=\frac{d'^2}{d^2}=\frac{28.2^2}{26.2^2}=1.16$$

Distance of source to screen	107 cm.
Distance of source to junction	109 cm.

$$\frac{R}{R'}=\frac{D'^2}{D^2}=\frac{109^2}{107^2}=1.03,$$

$$\frac{L}{R}=\frac{1.16}{1.03}\times\frac{L'}{R'}=1.12\times\frac{L'}{R'}.$$

In view of the great amount of work previously done by the method of the water cell it seemed desirable to examine the "water-bath" efficiency of the sources as well as the true radiant efficiency. Moreover, the latter is often difficult to measure directly as L is so small compared to R that it cannot be measured accurately. In this case the ratio of L/W was found as an intermediate value and multiplied by W/R to get the value L/R. L/W was determined in exactly the same way as L/R except that an 8-cm. water-bath was put in the path of the direct ray.

The "water-bath" efficiency is the ratio of the energy to which water is transparent to the total amount of energy radiated. The observed value W'/R is subject to two corrections.

1. The non-selective absorption and reflection of the water-bath. Photometric tests show this to be about 10 per cent. of the incident light.

2. The water-bath makes objects seen through it appear nearer by a distance of one fourth its thickness, 2 cm.

In cases where L/R is determined both directly and indirectly the two results may not quite agree. When this occurs the values are adjusted to divide up the error between them.

The Location of the Cut-off Screen.—There are two methods of locating the cut-off screen:

By looking through the window behind the radiomicrometer the spectrum $R-V$ can be seen. When using a source with a discontinuous spectrum such as the yellow flame arc the screen can be placed in the spectrum till its edge lies just beyond the last visible band, thus allowing all visible but none of the invisible radiation to pass. The spectrum of a white source can be made to appear as if it were discontinuous by placing a solution of a didymium salt before the slit S_1. A solution of crude "cereum oxide" containing about 20 per cent. didymium oxide was dissolved in hydrochloric acid and showed the following rather sharp absorption bands:

.680μ, .622μ, .578μ, .532μ, .520μ, .482μ, .476μ, .444μ, .427μ and transmission bands at .837μ and .770μ.

A spectroscope may be set up to examine the light passing through the radiomicrometer window. With a continuous spectrum the position of the cut-off screen can be followed with the spectroscope, and it can thus be moved to the correct position.

With point sources such as the carbon arc the cut off was very sharp, with discontinuous spectra like that of the yellow flame arc there is a wide dark space between the visible red and the infra-red, but with white extended sources such as the white flame arc the cut off is not sharp but may extend from .66μ to .7μ. This is because of the great slit width necessary.

Readings.—The radiomicrometer was used in connection with a lamp and scale. The scale was first set so its zero coincided with the image of the lamp filament, then by removing a screen the radiomicrometer junction was exposed to the radiation which it was desired to measure. The radiation was allowed to fall upon the junction until the instrument had reached the farthest point on the first swing, which was recorded. The screen was replaced at leisure. This is a much quicker procedure than to wait until the instrument has settled down to the final steady deflection.

The radiomicrometer was exposed alternately to the direct and to the modified radiation from the source. After ten readings of each had been made the photometric balance was readjusted and another set was made. In this way the effect of any drift in the radiant energy of the light from the source could be eliminated.

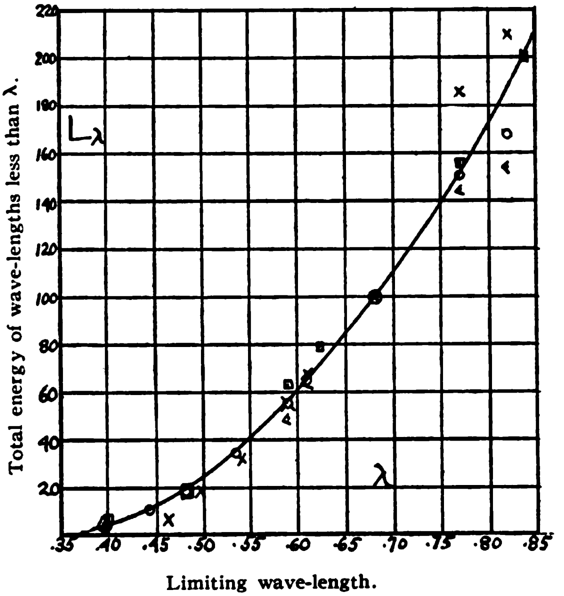

Fig. 12.

Besides the measurements of efficiency, determinations were made of the distribution of energy in the different parts of the visible spectra of the yellow flame arc, and the positive crater of the carbon arc. In both cases the determinations were made as for the measurement of *L* except that instead of comparing *L* with *R*, *L* was measured with different positions of the cut off screen. The results for the distribution of energy in the different bands of yellow flame arc are included in Table X. The distribution is such that three fourths of the visible energy is due to the red band and one fifth is due to the green band. The results with the positive crater are shown in Fig. 12, which is a curve between the limiting wave-length and the total energy made up of waves whose lengths are less than the limiting value.

The Mechanical Equivalent of Light.—To determine the mechanical equivalent of light it is only necessary to know the candle power of the source and the watts energy delivered within the limits of the visible spectrum. The data obtained include these values. The mechanical equivalent of light and its reciprocal, the light equivalent of radiation, will be found in Table XIII. These values for the light equivalent of radiation (21 to 39 candles per watt) are so much larger than those found by some of the previous workers that an experiment was made to determine directly what the value should be. As has been mentioned elsewhere Ångström's results recalculated on a basis of $.68\mu$ for the limit of visibility gave an efficiency of 21.3 candle power per watt for the Hefner lamp.

Charles V. Drysdale[1] examined the mechanical equivalent of white light from the arc lamp, from the Nernst filament, and also of yellow-green light. His values are 12.4, 8.4, and 16.7 candle power per watt.

P. G. Nutting[2] obtained a value of 13 candles per watt for yellow-green light but did not describe his method.

For the direct determination of the mechanical equivalent of light the assumption was made that an 8-cm. water-bath filled with a copper sulphate solution would transmit only visible light. The apparent candle power of the Nernst filament when viewed through this copper sulphate bath was determined, also the energy transmitted.

Apparent candle power through 8 cm. copper sulphate bath....................26.4 C.P.
Nernst filament 22.5 cm. from radio-micrometer, shining through bath. (Acts as if 20.5 cm. from instrument.)
Deflection..1.3 cm.
Energy .... .665 watts,
giving a value of .0252 watt per candle or 39.5 candles per watt. The color of the transmitted light is bluish green.

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[1] Proc. Roy. Soc., 80a, p. 19, 1907.

[2] Electrical World, 51, 1371, 1908.

Values Obtained with the Right Angle Arc.

The Positive Crater.

Table I.

Values by the prism train apparatus. Current 10 *amperes.*

	W' Direct through Water-bath.	L' Through Prism.	L'/W' Per Cent.	L/W Per Cent.	Correction.
1	34.25	12.86	37.5	41.8	×1.105 to ×1.12
2	37.41	13.90	37.1	41.5	
3	39.42	11.21	28.5	31.9	
4	34.27	12.45	36.3	40.7	
5	41.82	14.06	33.6	37.7	
6	44.48	17.36	39.1	43.8	
7	41.14	16.90	41.1	46.0	
8	37.54	14.32	38.2	42.2	
9	35.82	13.79	38.4	42.5	
10	35.84	13.41	37.4	41.3	
11	42.97	17.55	40.9	45.5	
12	36.08	17.32	48.0	53.8	
13	34.86	13.30	38.0	42.6	
14	52.90	23.10 (13 amps.)	43.7	48.7	
				42.9	

Table II.

Photometric measurements of arc.

Volts.	Amperes.	Watts.	Candle Power.	From Energy Input.	
				Watts per Candle.	Candles per Watt.
55	7.5	410	1,550	.265	3.8
	10	550	2,300	.240	4.2
	15	830	3,850	.215	4.65
	20	1,100	5,600	.195	5.1

Table III.

Results with water-bath.

Amperes.	Radiomicrometer Reading.		W'/R Per Cent.	W/R Per Cent.	Correction.
	R	W'			
7.5	12.43	2.11	17.0	18.5	×1.09
10	16.08	3.2	19.9	21.7	
15	21.86	5.26	24.1	26.2	
	27.48	6.79	25.4	27.6	
	22.72	5.70	25.1	27.3	
	24.45	5.94	24.3	26.5	
	24.47	6.09	24.9	27.1	
	24.72	6.02	24.3	26.5	
	21.23	5.36	25.2	27.5	
	23.52			26.96	
20	33.04	8.71	26.3	28.7	

The Negative Crater.

TABLE IV.

L/W Estimated.	W/R	L/R
40%	8.25%	3.3%

The Right Angle Arc; Alternating Current.

TABLE V.

Results with the prism train apparatus. Current 15 amperes.

W'	L'	L'/W' Per Cent.	L/W Per Cent.	Correction.
20.78	8.2	39.5	44.2	× 1.12
17.44	6.34	36.3	40.7	
19.98	6.91	34.6	38.8	
18.94	6.78	35.8	40.1	
18.52	6.51	35.1	39.4	
			40.64	

TABLE VI.

Candle power measurements.

Volts.	Amperes.	Watts.	Candle Power.	From Energy Input.	
				W.P.C.	C.P.W.
50	15	750	700	1.07	.94
50	20	1,000	1,200	.83	1.2

TABLE VII.

Results with water-bath.

Amperes.	R	W'	W'/R Per Cent.	W/R Per Cent.	R Watts Radiated.
		Lower carbon shaded.			457
15	9.37	1.53	16.4	17.77	618
20	12.66	2.44	19.25	20.9	
		Lower carbon unshaded.			590
15	12.08	1.74	14.36	15.61	
		Arc between the craters.			6.5 watts
	1.67	.335	20	21	.85 per cent. of crater

Table VIII.

The yellow flame arc. Entire arc.

L/W	R	W'	W/R	Correction.
50.4	46.8	12.51	29.2	× 1.087 Suspension constant 3,540 divs. per watt at one cm.
54.1	50.86	12.25	26.1	
68.9	52.32	12.98	27.0	
60.8	56.35	12.56	24.0	
55.8	53.62	13.16	26.6	
52.6	52.1	13.59	28.4	
64.5				
55.3				
55.7				
52.9				
57.1	52.0		26.9	R=430 watts

		From Energy Input.	
Amperes	13.5	Watts per candle	.23
Volts	44.5	Candles per watt	4.3
Watts	600		
Candle power	2,580		

Table IX.

The yellow flame arc. Arc stream.

L/W Per Cent.	W/R Per Cent.	L/R Per Cent.	L/R Calculated.
78.5	48.5	35.8	
		39.8	
76.0	47.0	32.5	
		47.5	
73.5	49.7	45.9	
		45.6	
72.1	49.3	49.1	
		35.4	
78.8	50.5		
81.0			
Found 76.8	49.0	41.45	37.60
Adjusted values 79	49.5	39	

Table X.

Distribution of energy in the different bright bands of the spectrum of the arc stream.

100 per cent. is the energy of the visible part of the spectrum.

Energy which gets through water-bath	126 per cent.
Luminous energy; red + blue + green	100
Green + blue	25.5
Blue	5.0
Green	20.5
Red	74.5
Infra-red which gets through water-bath)	26
Red + infra-red	100.5

TABLE XI.

The white flame arc. Entire arc.

L/W Per Cent.	R	W'	W'/R Per Cent.	W/R Per Cent.	Correction.
44.4	56.93	16.28	28.6	31.1	×1.087
45.7	59.45	17.41	29.4	32.0	
45.3	57.35	16.42	28.7	31.2	
47.3	56.72	16.94	29.9	32.5	
46.0	57.76	17.14	29.7	32.3	
45.58	57.64	=476 watts		31.82	

		From Energy Input.	
Amperes	13.5	Watts per candle	.44
Volts	47	Candles per watt	2.27
Watts	635		
Candle power	1,440		

TABLE XII.

The white flame arc. Arc stream only.

L/W Per Cent.	W/R Per Cent.	L/R Per Cent.	L/R Calculated. Per Cent.
54.3	50.5	27.85	27.4
Adjusted values 54.5	50.5	27.5	

Probable Accuracy of Results.—No very exact results with arc lamps are possible on account of the wide fluctuations continually occurring in their behavior, hence it is necessary to be content with a rather rough approximation.

With the apparatus used in the present investigation there are apparently no inherent instrumental errors of greater magnitude than the settings for photometric equality.

ÅNGSTRÖM'S RESULTS.

In his paper on "Energy in the Visible Spectrum of the Hefner Standard,"[1] Ångström determined the following:

The distribution of energy in the infra-red.

The percentage of the total energy of wave-length less than $.76\mu$; L_{76}/R.

The value of L_λ for various wave-lengths. (The energy of the light of all wave-lengths less than λ.)

From this, the distribution of energy in the visible part of the spectrum.

These last two were expressed in the form of curves.

---

[1] Phys. Rev., 17, 302, 1903, Nova Acta, Royal Society of Science, Upsala, 3d series, Vol. XX.

TABLE XIII.

Summary of results.

Source.	Amps.	C.P.	L/W Per Cent.	W/R Per Cent.	L/R Per Cent.	Watts.		As Radiated.		At 100% Eff.	
						R	L	W.P.C.	C.P.W.	W.P.C.	C.P.W.
Carbon arc	7.5	1550		18.5	7.9	607	48	.39	2.6	.031	32
	10	2300	42.9	21.7	9.3	785	73	.34	3.0	.032	31
+ Crater....	15	3850		27.0	11.6	1148	133	.30	3.4	.035	29
	20	5600		28.7	12.3	1614	199	.29	3.5	.036	28
											30
−Crater		(est.)	40	8.25	3.3						
A. C.											
Shaded....	15	700	40.7	17.8	7.2	457	33	.65	1.5	.047	21
	20	1200		20.9	8.5	618	53	.51	2.0	.044	23
Entire	15	700		15.6	6.3	590	37	.84	1.2	.053	19
											21
Arc stream..				21		6.5					
Flame arcs											
Entire arc											
Yellow....	13.5	2580	57.1	26.9	15.4	430	66	.17	6.0	.026	39
White.....	13.5	1440	45.7	31.8	14.6	476	69	.33	3.0	.048	21
Arc stream											
Yellow....	13.5		79	49.5	39						
White.....	13.5		54.5	50.5	27.5						
Nernst through											
copper sulphate		26.4			100		.665			.025	39.5
Hefner (Ångström)		.9			.363	11.3	.032	12.3	.08	.047	21.3

The value of L_{76}/R for the Hefner is .96 per cent.

By reference to the curve the value of L_{68}/L_{76} is .389, giving $L_{68}/R =$ .373 per cent.

The total radiation at the distance of one meter is 214×10^{-7} calories per square centimeter per second.

Assuming uniform spherical distribution this gives a value of 11.28 watts as the total radiation.

The value $L_{76}/R = .96$ per cent. gives for the mechanical equivalent of light .1085 watt per Hefner, .1205 watt per candle[1] or 8.3 candles per watt.

The value of $L_{68}/R = .373$ per cent. gives .0422 watt per Hefner, .0469 watt per candle or 21.3 candles per watt.

Although the removal of the light between .76μ and .68μ has a large effect on the energy radiated it has but a slight effect upon the illumination given by the lamp.

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[1] Hefner = .9 candle power.

The author wishes to express his appreciation of the facilities offered by the department of physics and his gratitude for the help and encouragement given by his fellow students and by the staff.

SUMMARY.

The *A* line .76μ is not a suitable point to take for the limit of the visible spectrum.

Examination of luminosity curves shows that it would be preferable to assume this limit to be at .68μ.

If all radiation of greater wave-length than .68μ be removed the resulting decrease in light can be neglected.

The measurement of radiant energy was made with a radiomicrometer. The kick or ballistic method was used. The kick is proportional to the final deflection and to the energy.

The calibration of the radiomicrometer in absolute units using the Nernst filament and the Hefner lamp showed a general agreement between the energy of the Nernst filament as calculated from the energy input and as derived from Ångström's value of the radiation from the Hefner lamp.

A modification of the method of Ångström was used to determine the radiant efficiency of the right angle carbon arc, the yellow flame arc, and the white flame arc.

The greatest efficiency was found in the arc stream between yellow flame carbons, the carbon tips being shaded. With this arc the light energy constitutes 39 per cent. of the energy radiated.

The highest efficiency from black body radiation is from the positive crater of the carbon arc. An efficiency of from 8 to 12 per cent. may be expected from this source.

Calculations of the mechanical equivalent of light from these data show that one watt can produce as high as 30 candle power of white light and 39 candle power of orange light (yellow flame arc). This is much higher than has been previously supposed except from the data of Ångström which give 21.3 candle power per watt when recalculated for the limit .68μ.

CORNELL UNIVERSITY,
ITHACA, N. Y.,
June, 1911.

THE TRANSMISSION OF SOUND THROUGH POROUS AND NON-POROUS MATERIALS.

BY C. S. MCGINNIS AND M. R. HARKINS.

THE object of this investigation was to study more extensively the nature of sound transmission through porous and non-porous materials and to quantitatively determine the transmitted intensity. Up to the present time little attention has been given to the experimental phase of the subject. It was determined in 1901 by Tufts[1] that "The resistance offered by granular materials to the to-and-fro motion of the air particles in a sound wave is proportional to the thickness of the material, other things being equal." Also "Observations were made upon the transmission of sound and of direct currents of air through porous materials of a woven texture. The results showed that the resistance which such materials offered to the transmission of sound and direct currents of air was directly proportional to the thickness or number of layers of the material used, as was the case with granular materials."

Weisbach[2] working along similar lines arrived at the following conclusion: The acoustic transmission and reflection of thin sheets are not easily measured because the vibrations of the sheet as a whole often complicate and obscure the sound otherwise transmitted. If one eliminates these swings, as far as possible, then one arrives at a result which agrees with theory, namely, that the transmission and reflection for given wave-lengths depend only on the mass per unit area of the sheet.

APPARATUS.

The source of sound was an open organ pipe, pitch 768 complete vibrations, with pressure supplied by a motor-driven centrifugal blower and controlled by a pressure regulator. In the path of the stationary sound waves was placed a telephone receiver *P*, which was connected through a capacity *C*, to the primary of a transformer *T*.

The secondary of the transformer was connected in series with a resistance *R*, a Siemens and Halske direct current, high sensibility galvanometer *G*, and a crystal rectifier *M*. This sound detector was devised by G. W. Pierce.[1]

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[1] Transmission of Sound through Porous Materials, Am. J. of Sc. (4), 11, 1901, p. 357.

[2] Versuche über Schalldurchlässigkeit, Schallreflexion, und Schallabsorption, Ann. d. Phys., 14, p. 763, 1910.

Preliminary experiments showed conclusively that a telephone transmitter with battery, although extremely sensitive, could not be relied upon for quantitative results. The telephone receiver, more constant in its action although less sensitive, was therefore employed. A number of receivers were tried before one of sufficient sensitiveness was found. The one finally employed was of the Stromberg Carlson type which was so constructed as to respond best to variation in pressure, that is, at the node of the stationary wave. In order that the sheets of material could be conveniently exposed before the mouth of the receiver and that the incident sound could have no other access to the diaphragm than through the material, the receiver was encased in a thick lead tube closed at one end.

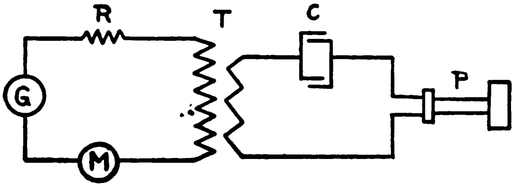

Fig. 1.
Receiving circuit.

A one to twenty step-up transformer gave best satisfaction for the particular constants in the circuit. Its primary resistance was 5.7 ohms and secondary resistance 850 ohms. In order to determine the best magnitude of capacity, a resonance curve was taken. This curve showed that 0.2 micro-farad gave the highest deflection for the particular pitch used.

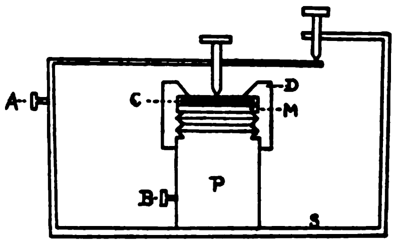

Fig. 2.
Mounting for crystal.

The crystal rectifier mounting, with terminals *AB* is shown in Fig. 2. A threaded, cylindrical, brass pillar *P* supports a sheet of mica *M*, which in turn supports the crystal *C*. The screw cap *D* holds the crystal in position. A hard-rubber base *S* supports the brass pillar and also the two metal posts which carry the regulating screws. A mutual adjustment of these screws produces any desired pressure on the crystal. Crystals of molybdenite proved to give sufficient rectification and were used throughout the research, but satisfactory ones were obtained only after many trials. Even for one particular pressure the percentage rectification did not remain constant for any great length of time, so that it became necessary after each reading to check the original reading by an additional observation. Oftentimes a tedious manipulation of the pressure was necessary to maintain a proper deflection.

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[1] A Simple Method of Measuring the Intensity of Sound, Proc. Am. Acad., XLIII., No. 13, 1907.

CALIBRATION.

The calibration consisted in finding the relation between the intensity of the incident sound and the deflection of the galvanometer. The intensity of the sound source was kept constant by regulating the air pressure which was indicated by a water manometer. The intensity of the sound incident on the diaphragm of the receiver was varied by the use of lead plates containing circular apertures of different diameters. The galvanometer showed no deflection when a lead plate was clamped over the end of the lead casing containing the receiver. The clamping was done as follows: A flat brass ring was permanently fixed to the end of the lead casing. A similar brass ring was screwed to the first one and between them the lead plates were held in position. The circular apertures of the lead plates were small compared to the size of the diaphragm so that allthe energy passing through the openings was incident near the center of the diaphragm. Hence the intensity of the incident sound was directly proportional to the area of the aperture. A reversion to the $\frac{3}{8}$-inch aperture after each observation checked the constancy of the crystal. Fig. 3 shows that the deflection of the galvanometer is directly proportional to the area of the aperture and hence to the intensity of the incident sound. For apertures as large or larger than the diaphragm opening the law no longer holds.

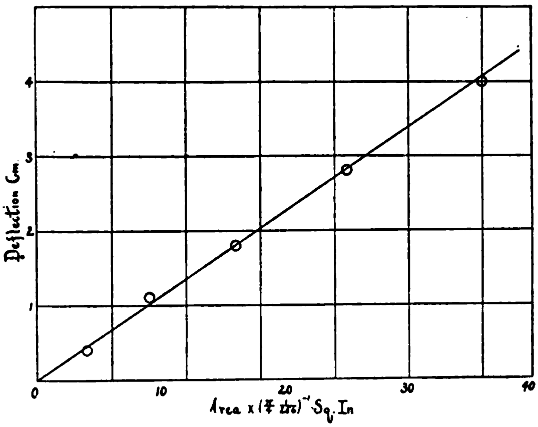

Fig. 3.

Observations and experimental details.

Preliminary experiments showed conclusively that the method of clamping the materials investigated influenced to a high degree the percentage of sound transmitted. A more thorough study of the matter showed that different methods of clamping produced different degrees of lateral vibrations. Thus a special method of clamping was devised which practically eliminated the lateral vibrations. Until this was done it was impossible to procure results which were independent of the clamping pressure and the tension in the specimen. Fig. 4 shows the clamp employed.

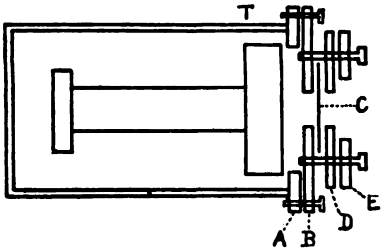

Fig. 4.
Device for damping lateral vibrations.

A is a flat brass ring 0.2 cm. thick and 6 cm. internal diameter which is fastened permanently to the end of the lead tube *T*. *B* is a brass plate 0.15 cm. thick with aperture ½ inch in diameter. *C* is the specimen and *D* is a lead sheet 0.05 cm. thick with ½-inch aperture. *E* is a brass ring 0.35 cm. thick with 1-inch aperture.

Since the galvanometer registered a maximum deflection when the receiver was placed in a node of the stationary wave, that position was employed in all observations. The following substances were investigated, namely, blotting paper, wrapping paper, roofing paper, oil cloth, tin-foil, asbestos, curtain material, lawn, longcloth, percale, cretonne, curtain scrim, linen, calico, felt, velvet, copper wire gauze, mica and aluminum.

In order to explain definitely how the lateral vibrations of the material affected the observations we will confine our discussion to oil cloth which is non-porous, that is, does not allow air currents to pass through. Fig. 5 shows the relation between the percentage transmitted and number of sheets when the apertures in *D* and *E* of Fig. 4 were large, so that the oli cloth was clamped only at the outer edge.

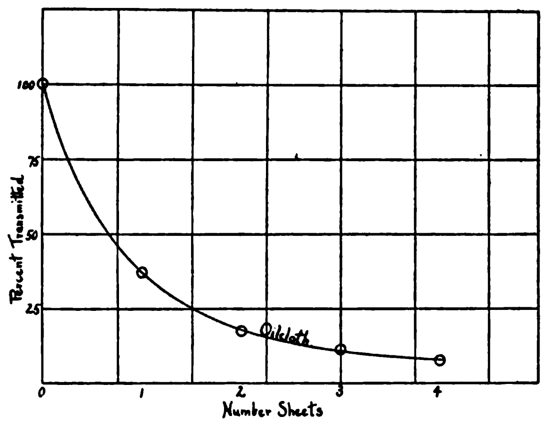

Fig. 5.

It is to be noted that the percentage transmitted ranges from 37 per cent. for one sheet to 7.5 per cent. for four sheets. When a lead plate was used in place of oil cloth the galvanometer deflection was zero, showing that there were no leaks. Fig. 5 is in very close agreement with results obtained by Weisbach for oil cloth of a similar mass per unit area, namely, 0.034 gram per sq. cm. When the oil cloth was clamped exactly as shown in Fig. 4 and when the open deflection was 4 cm. as was the case in Fig. 5, the galvanometer showed no deflection, thus indicating that the transmission as shown in Fig. 5 was due to the oil cloth being set in vibration and acting as an independent vibrating source. This discrepancy is of great significance and will be discussed later. Other non-porous substances or those nearly so, acted in a similar manner. Roofing paper, wrapping paper, asbestos, blotting paper, curtain material, tin foil, mica and aluminum transmitted either zero or considerably less than one per cent. The more porous substances of woven texture, were used to determine the relation between the intensity transmitted and the number of sheets. Table I. shows the numerical results.

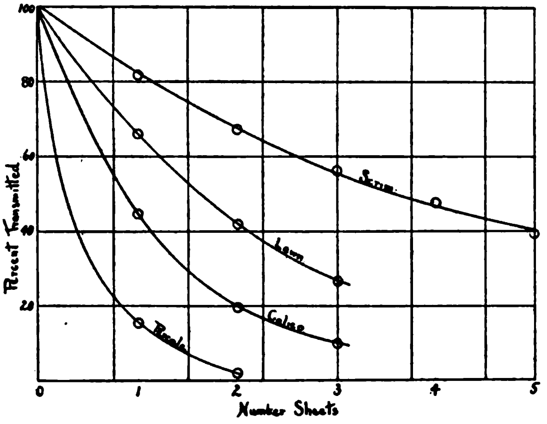

Fig. 6.

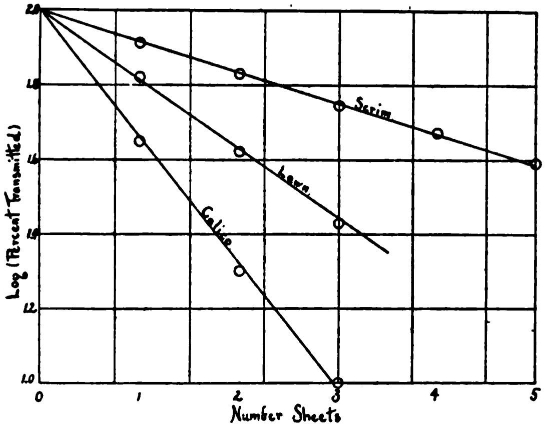

Fig. 7.

The curves for calico, percale, curtain scrim and lawn, showing the relation between number of sheets and percentage transmitted, are shown in Fig. 6, while the relation between number of sheets and logarithm of percentage transmitted, is shown in Fig. 7.

Table I.

Material.	$\frac{\text{Mass}}{\text{Area}}$ in $\frac{\text{gms.}}{\text{cm.}^2}$	Per Cent. Transmitted.	Material.	$\frac{\text{Mass}}{\text{Area}}$ in $\frac{\text{gms.}}{\text{cm.}^2}$	Per Cent. Transmitted.
Lawn.			*Longcloth.*		
1 sheet	0.00537	65.9	1 sheet	0.00984	27.6
2 sheets		41.8	2 sheets		7.6
3 sheets		26.7	*Cretonne.*		
Calico.			1 sheet	0.0120	27.8
1 sheet	0.00868	44.5	2 sheets		15.5
2 sheets		19.7	3 sheets		11.8
3 sheets		10.0	*Linen.*		
Percale.			1 sheet	0.0129	6.3
1 sheet	0.0121	15.3	*Linene.*		
2 sheets		2.0	1 sheet	0.0167	2.0
Curtain scrim.			*Felt.*		
1 sheet	0.0051	81.6	1 sheet	0.0266	1.6
2 sheets		67.2	*Velvet.*		
3 sheets		56.1	1 sheet	0.0158	1.6
4 sheets		47.5	*Copper wire gauze.*		
5 sheets		39.1	1 sheet	0.102	76.4
			2 sheets		58.6

Discussion of Results.

It is readily seen from the results that non-porous substances such as oil cloth, paper, tin foil, etc., do not transmit sound when the lateral vibrations are eliminated, at least in so far as our apparatus will detect. This would limit the transmission to a very small fraction of one per cent. Porous substances, on the other hand, do transmit a considerable percentage of incident sound, the percentage depending upon the diameter, length and nature of the channels. Inspection of the materials would lead one to expect a much greater transmission than was found. The general law appears to be

$$I = I_0 e^{-kn}, \tag{1}$$

$$\log\frac{(I)}{(I_0)} = -kn, \tag{2}$$

where I = transmitted intensity,
I_0 = incident intensity,
n = number of sheets,
k = constant.

All substances investigated agreed with this law with the exception of cretonne which proved to be a decided exception. In cretonne the channels are not so definite and clear cut as in the other cases. The exponential form of equation (1) suggests at once that whatever sound is transmitted goes through the pores. This would immediately suggest an investigation of the channel action. Preliminary experiments on a single channel of diameter 3/16 inch, in lead plates, showed that the percentage transmitted, as the length of the channel was changed, agreed with the above law very closely. This matter will be further investigated.

Our results differ widely from those of Weisbach who attempted to apply Rayleigh's[1] formula for the amplitude[2] of the sound reflected from thin plates, namely,

$$-\frac{\frac{\pi\rho_1 l}{\rho\lambda}}{\sqrt{1+\pi^2\left(\frac{\rho_1 l}{\rho\lambda}\right)^2}}, \tag{3}$$

where l = thickness of plate,
ρ = density of first medium,
ρ_1 = density of second medium (plate),
λ = wave-length.

When the first medium is air and the pitch 768 double swings, as used in our experiments, formula (3) may be written

$$I_r = I_0\frac{\rho_2^2}{.00034+\rho_2^2}, \tag{4}$$

where I_r = reflected intensity,
I_0 = incident intensity,
ρ_2 = mass per unit area of the plate.

If there is no absorption the transmitted intensity I_t will be $I_0 - I_r$,

$$I_t = \frac{.00034}{.00034+\rho_2^2}. \tag{5}$$

Weisbach's results did not agree with Rayleigh's theoretical values but could be brought into approximate agreement by shortening the ordinates by a large constant factor. He did not fulfill the conditions imposed by the formula. For a statement of these conditions and a complete interpretation of the formula we are indebted to Baron Rayleigh.

The formula applies to the reflection of plane waves incident normally on a free and thin lamina which lamina is incompressible as compared with the first medium and is completely uniform in its mechanical properties. The lamina acts as a body possessing inertia under the pressures of the three waves, incident, reflected and transmitted Experimentally it would be almost impossible to satisfy the requirement of freedom. However a membrane such as oilskin spread over a large enough hoop might possibly satisfy the requirement, *i. e.*, that the motion shall be independent of any tension due to the outside fastening. The vibrations which Rayleigh's formula permits are those controlled by the inertia of the membrane and the elasticity of the air and not those which depend on the elastic constants of the material. Therefore Weisbach should not have applied Rayleigh's formula in any case, since the condition of freedom was not satisfied.

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[1] Theory of Sound, Vol. II., p. 88.

[2] Note misprint in Rayleigh, Vol. II., p. 88, of intensity for amplitude.

We also wish to emphasize the fact that formula (5) cannot be applied to our results, even to those substances such as tin foil, paper, mica, etc., whose mechanical properties are uniform, since the condition for freedom is not satisfied. In any case it cannot be applied to porous substances. If the lateral vibrations are damped the substances which are uniform in their mechanical properties should act as a fixed wall, namely, reflect all incident sound. This is conclusively shown by our results.

Weisbach's results could not be expected to agree with ours since his membrane was not thoroughly damped while in our case the lateral vibrations were completely eliminated. Our results verify the latter statement. For non-porous substances or those nearly so as paper, oil cloth, curtain material, etc., we found the transmission to be either zero or a small fraction of one per cent., while Weisbach found from 30 to 60 per cent. For porous substances such as linen, calico, lawn, etc., we likewise found a much smaller percentage transmitted.

Summary.

1. The crystal rectifier, with apparatus as described, is reliable when used for the comparison of sound intensities but cannot be used for absolute determinations since the percentage of rectification is liable to change.

2. For non-porous substances or those nearly so, the intensity of sound transmitted is either zero or considerably less than one per cent.

3. For porous substances of woven texture the general law for the transmitted intensity is $I_t = I_0 e^{-kn}$, *i. e.*, each sheet transmits a definite percentage of the sound incident upon it.

4. Most of the sound which is commonly said to be transmitted is due to the lateral vibrations of the material as an independent sound source. The intensity actually transmitted depends upon the size and nature of

the pores, *i. e.*, absorption is the predominating factor. This is in agreement with Tufts' general idea as previously stated, namely, that the transmission of sound depends definitely upon the facility with which the substance transmits currents of air.

In conclusion we wish to thank Professors H. C. Richards and R. H. Hough for their valuable suggestions and coöperation.

Randal Morgan Laboratory of Physics,
University of Pennsylvania,
May 1, 1911.

THE SELECTIVE REFLECTION OF ORTHO-, META- AND PYRO-PHOSPHATES IN THE INFRA-RED SPECTRUM.

BY GRACE LANGFORD.

IT is well known that the reflecting power of certain non-metallic substances varies widely in different parts of the infra-red spectrum. For example, the reflecting power of quartz[1] is practically zero for radiations of wave-length 7.4μ and rises abruptly to 75 per cent. at 8.45μ. The work of Coblentz[2] and Morse[3] shows that not only may carbonates, nitrates and sulphates be distinguished from each other by their selective reflection alone, but also that of the salts of any one acid, those with the heavier bases may in general be separated from those with the lighter, the valence of the bases being the same in all. There was little evidence on salts having a common acid-forming element to show either the effect of a change in the valence of the base, or the effect of a change in the ratio of the weight of the acid forming element to the weight of oxygen combined with it in the acid radical. The series of substances which seemed best adapted to a study of these effects were not obtainable in a form suitable for examination by the usual methods. This paper describes a method by which one may obtain an indication of the selective reflection characteristic of those salts which cannot be had in large crystals. This method has been applied to the examination of sixteen of the ortho-, meta- and pyro-phosphates, and the results are given in the following pages.

PREPARATION OF SURFACES.

A large number of the phosphates were obtainable only in the form of powder precipitates. A few were in the form of minute crystals and one only, sodium meta-phosphate, in a solid mass. On this last a surface large enough for the purpose was polished by rubbing on a surface of ground plate glass. Since the melting point of most phosphates is very high it was impracticable to melt them into solid cakes. The possibility of obtaining reflecting surfaces by the compression of powders was first suggested by Mr. Eimer, of Eimer and Amend, and the practical details of the following process were devised by Dr. E. F. Nichols and Dr. W. S.

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[1] PHYS. REV., 1897.

[2] Investigations of Infra-red Spectrum, Parts III. and IV., 1906; V., 1908.

[3] Astrophysical Journal, 26, p. 225, 1907.

Day. In Fig. 1, *B* represents a block of hardened and polished steel to which the steel rings, *C* and *C′*, could be tightly screwed. *A* is a steel piston, which slips easily in the rings. The ring *C* contains the powder to be pressed and *C′* acts merely as a guide for the piston. The steel block was ground with emery and water and polished till the top had a fine mirror surface. The rings having been screwed to the block, the lower one, *C*, was filled with the powdered salt and the piston inserted on top of the powder. The piston head was then subjected to a pressure of 42,000 to 52,000 pounds per square inch.[1] After releasing the pressure and withdrawing the piston the steel block was carefully separated from the rings, leaving in the lower ring a solid cake of the compressed powder which sometimes had a very brilliant mirror surface copied from the surface of the polished steel block. In some cases a better surface could be formed by forcing the cake out of the ring and carefully polishing it in the ordinary way. The salts used were obtained as free from water as possible. To drive off any moisture which might be held in the precipitates and in the case of Na_3PO_4, to drive off water of crystallization, the substances were heated over a sand-bath. Unless the powder were very fine it was ground in a mortar and after drying was sifted through graded sieves. The finest powder, that passing the 200 per inch mesh, was put in the rings first, that it might form the surface and the coarser parts were used for the main bulk of the cake. When only a small quantity of substance was available it was put in the ring first and the rest of the cake made of a different substance. Only three of the substances used showed any crystalline structure even under the high power microscope. Of these Na_3PO_4 lost its crystalline form with the water of crystallization. The other two, $Zn_3(PO_4)_2$ and KPO_3 remained unchanged when heated.

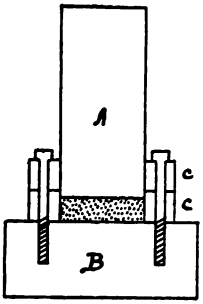

Fig. 1.

The surfaces obtained by pressure against a plane surface in this way were rather convex, probably a result of the bulging of the powder after the pressure was removed. Sometimes the cake cracked, due to the strain. As most of the pressed cakes of the phosphates were not hard enough to be ground plane and polished, an effort was made to reduce the convexity by pressing on a slightly convex steel surface. But as no two surfaces had the same convexity even when the same pressure was used it was impossible to predict just what curvature would result in any given case or to wholly correct it. With these curved surfaces the absolute reflecting power was not obtained. But since other conditions made it impossible and as relative values answer our purpose this lack of planeness was not very important. Also the collecting mirrors used in the examination were large enough to receive the beam even if its divergence were slightly increased by the curvature of the salt's surface. Approximately absolute values might at any time be obtained by determining the values at a few wave-lengths distributed along the spectrum and deducing the whole reflection curve from the relative values at the selected wave-lengths. The cakes of the various substance when pressed differed much in appearance and structure. Aluminum and magnesium phosphates, $AlPO_3$ and $Mg_3(PO_4)_2$, for example, in the form of white powder looked alike. After pressing, the $AlPO_4$ had the appearance of fine white porcelain and was brittle and chipped off in layers like slate, and the surface was very brilliant. But $Mg_3(PO_4)_2$ gave a dull surface and showed no pronounced structure.

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[1] The pressures were obtained at first by the use of the testing machine in the mechanical engineering laboratories through the kindness of Professor Ira H. Woolson and Mr. J. S. Macgregor. Later a hydraulic press was used in the physics laboratory.

GENERAL PLAN OF APPARATUS.

The mirror M (Fig. 2) forms an image of the source, N, on the reflecting surface under examination at S. The reflected beam is brought to a focus by the mirror M_2 on the collimator slit C of spectrometer. After passing the slit the beam is rendered parallel by the spectrometer mirror, M_3, and is then resolved by the prism P, and reflected by the plane mirror M_4. The portion of the spectrum falling on the second spectrometer mirror M_5 is brought to a focus on the slit, T, which replaces the usual cross wires of the observing telescope of the spectrometer. The energy passing through the slit falls upon the concave mirror, M_6, and is concentrated on the vane of the radiometer, R.

There are several reasons for forming an image of the source N on the reflecting surface S. In the first place the adjustments are more easily made. Secondly, a smaller surface may be used without loss of energy, and the curvature of the reflecting surface over a small area is likely to be more regularly than over a large one. Moreover, it was possible to choose the best part of the surface, thus avoiding the edges and flaws.

DETAILS OF APPARATUS.

Source.—A Nernst glower, 110 volts and 0.8 ampere, fed by a 120-volt storage battery served as a source. The glower was protected from air currents by an asbestos shield. An ammeter and variable resistance in circuit made it possible to hold the glower current constant in spite of slow fluctuations in the battery voltage and to detect any sudden change likely to cause error. After adjustment the current usually remained very constant throughout a series of observations.

Spectrometer.—A Schmidt and Haensch spectrometer with Rubens attachment, belonging to the Rumford Committee of the American Academy of Arts and Sciences was used. In place of the customary simple prism the spectrometer table bore the Wadsworth mirror prism arrangement[1] and the different parts of the spectrum could therefore be caused to fall upon the slit T (Fig. 2) by rotating the prism table, the arms of the spectrometer remaining fixed. The spectrometer mirrors M_3 and M_5 had each a focal length of 35 cm. and an aperture of about 4 cm.

Prism.—The sylvite prism P had faces 3.2 cm. high and 2.5 cm. broad, and a refracting angle of 38° 9′ 51″. Wave-lengths to 20μ may be determined with a sylvite prism of this refracting angle so that the field of observation was extended considerably beyond the limit reached with ordinary 60° rock-salt prism. In order to interpret spectrometer sittings in terms of wave-lengths a curve was drawn with wave-lengths as abscissas and as ordinates, one half the difference between the angles of minimum deviation for the given wave-length and for the sodium line. One half the angle was taken, since with the Wadsworth prism and mirror arrangement the angle of rotation of the prism table is equal to one half the change in the angle of minimum deviation. The values for the angles of minimum deviation for wave-length from $.5\mu$ to 20μ at intervals of $.5\mu$ were calculated from the Ketteler-Helmholtz dispersion formula using the constants for sylvite determined by Rubens.[2] The adjustment of the spectrometer was repeatedly checked by observing the reading of the spectrometer scale when the B line coincided with the telescope slit. The curve for wave-lengths and spectrometer settings was tested by observing the wave-lengths of maximum reflection for quartz and calcite which agreed within experimental errors with the values found by other observers.

Radiometer.—A Nichols radiometer with a sylvite window was used. The mica vanes measured 5 mm. × .75 mm. and were placed with their outer edges 8 mm. apart. The faces of the vanes were covered with a thin layer of platinum black held on by shellac. The radiometer stood on a shelf supported by a thick inner wall, and under ordinary conditions the vibrations of the building did not affect the readings. Deflections of the radiometer vanes were determined by observing the position of the image of the index lamp, formed on the scale one meter distant, by a small concave mirror fastened at the lower extremity of the suspended system.

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[1] Phil. Mag., 38, 337, 1894.

[2] Wied. Ann., 60, 418, 1897; 60, 724, 1897.

Adjustment of the Surface.—The surface to be examined was clamped behind one of the openings, S_2 (Fig. 2), in an upright brass plate mounted on a small car which slid smoothly on the carefully planed ways of a bedplate. At a second opening, S_1, was placed a plane silvered mirror used as a standard reflector. The back of the upright plate was plane so that either the surface whose reflection was to be studied or the standard could be brought successively into the same position by sliding the car along the ways between properly adjusted stops. In the case of plane bright surfaces this adjustment was tested by observing in a telescope provided with cross wires, the position of the image of an incandescent lamp filament reflected first from one and then from the other surface. The adjustment of the more brilliant surfaces was made slightly more exact by the use of three screws which passed through the upright plate and pressed against the silver surface, making it possible to change the angle of the silver until it was in the same plane with the other surface. The adjustment required was in each case so small that but a slight error was introduced by not making the finer adjustment for the duller surfaces after they were clamped in place.

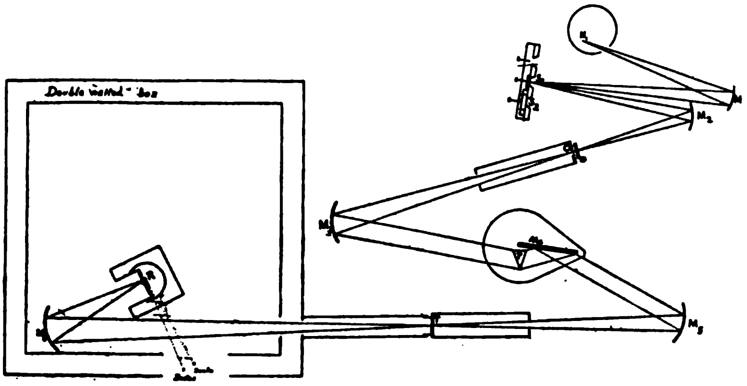

Fig. 2.

Purification of the Spectrum.—In the preliminary work the energy in the region 18μ to 20μ was found to be unexpectedly great, and it was suspected that this was due, in part at least, to stray energy of shorter wave-lengths. To test this, observations were made on the transparency of quartz, fluorite and rock salt at 20μ where these salts, in plates of the thickness used, were known to be almost entirely opaque. It was found that of the apparent energy at 20μ 70 per cent. was transmitted by quartz, 78 per cent. by fluorite, and 82 per cent. by rock salt.

Of the remaining 18 per cent. not transmitted by rock salt, perhaps 5 to 12 per cent. might be accounted for by diffuse[1] reflection from the surface, and this might also consist of short waves. Therefore, only a remainder of not more than 13 per cent. of the total energy could be considered to be of wave-length 20μ. To get rid of as much as possible of this stray energy, shutters of the three above-mentioned substances were mounted so that either one could be placed in front of the collimator slit at D (Fig. 2). Between 4μ and 10μ a plate of quartz 3.5 mm. thick was used, between 10μ and 17μ a plate of fluorite 3 mm. thick, and beyond 17μ a plate of rock salt 4 mm. thick. In the last part of the work the quartz plate was being used for other purposes and a piece of plate glass made a satisfactory substitute.

Method of Making Observations.—When the shutter was in front of the slit, C, the energy to which the shutter was transparent produced a deflection of the radiometer suspension and the position of the spot of light on the scale was read. When the shutter was raised the additional deflection was that due to the energy which the shutter formerly cut out and the turning point of the index image on the scale gave a second reading. The shutter was lowered as soon as the extreme swing was reached and the turning point on the backward swing was used. The difference between the second reading and the mean of the first and last is proportional to the energy of the wave-length for which the spectrometer was set and for convenience is called the deflection. The usual order of observing was to take first such a set of readings with the silver surface in the reflecting position. This was followed by three or more sets in which the surface being studied replaced the standard silver surface. In order to make sure that the energy from the Nernst glower had remained constant, a second set of observations was made on the silver surface. If the deflection differed from the first, or if the deflections were small, more observations were made. When the deflections were small the time of a large deflection was determined and the same time allowed between removing or replacing the shutter and reading the scale. Assuming the reflection of silver to be total[2] the ratio of the average deflection with the salt surface in place to that with the standard silver surface in place is called the percentage of reflection. The slit widths were varied from .1 mm. at 4μ corresponding to an interval of $.23\mu$, to 1 mm. corresponding to an interval of $.43\mu$ at 20μ. Care was taken to make no changes in the material used for a shutter, or in the slit widths, at a part of the spectrum where the percentage of reflection was changing rapidly.

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[1] Pogg. Ann., 138, 174, 1869.

[2] E. Hagen and H. Rubens, Ann. die Phys., II., 73, 1903.

The results are plotted in the accompanying curves in which wave-lengths are chosen as abscissas and percentages of reflection as ordinates. Of the sixteen substances examined ten were ortho-phosphates, two meta-phosphates, and four pyro-phosphates, the typical formulas being respectively R_3PO_4, RPO_3 and $R_4P_2O_7$, where R represents a monovalent base.

Ortho-Phosphates.

The reflection curves for the ortho-phosphates are shown in Figs. 3 and 4. The maxima occur in two distinct parts of the spectrum, one between 9μ and 11μ which for convenience will be referred to as the first region, and the other beyond 16μ or in the second region of maximum reflection. Between these two regions there are no reflection maxima. The curves for the three ortho-phosphates having monovalent bases are put together in Fig. 3. They seem to form a typical set showing clearly that the first point of maximum reflection occurs farther toward the long waves as the atomic weight of the base increases (at. wts. Li = 7, Na = 23, Ag = 108). Of all the salts examined Ag_3PO_4 has the highest and Li_3PO_4 the next highest percentage of reflection. The bases of these two are monovalent and belong to the same chemical group. That the high reflection cannot be attributed to this is shown by the fact that though sodium is also in this group the reflecting power of Na_3PO_4 is one of the lowest. A fourth member of this chemical group, K_3PO_4, was so deliquescent that it was impossible to examine it. All three curves for this monovalent series have two maxima in the second region, each of the two for Ag_3PO_4 being at longer wave-lengths than the corresponding one for Li_3PO_4. But the second for Na_3PO_4 is at a shorter wave-length than the second for Li_3PO_4.

The ortho-phosphates with divalent and trivalent bases are represented by the curves in Fig. 4. They are arranged in the order of the weights of the bases combined with one atomic weight of phosphorus beginning at the bottom with the smallest weight. When the weight of the base is changed these show in general a change in the first region wave-length selectively reflected, similar to that observed in the case of the monovalent series. $Zn_3(PO_4)_2$, and perhaps $Sr_3(PO_4)_2$ with two maxima, are exceptions. There is less regularity in the change of position of the maxima in the second region and the reflection bands are in general more complex. There seems to be no very distinctive difference between the curves for the monovalent and divalent ortho-phosphates. The bases in the latter series—magnesium, calcium, zinc, strontium and lead—belong, with the exception of lead, to the second chemical group. $Sr_3(PO_4)_2$ and $Mg_3(PO_4)_2$ have each two points of maximum reflection in the first region. There is a rather doubtful indication of a second maximum on the left slope of the first band in $Zn_3(PO_4)_2$ but none with $Ca_3(PO_4)_2$. The general form of the curve for $Pb_3(PO_4)_2$ is very similar to the others, although lead belongs to a different chemical group.

Only two representatives of the ortho-phosphates with trivalent bases could be obtained, $AlPO_4$ and $BiPO_4$. An effort was made to add BPO_4 to the list, but it proved unstable at a certain stage in its preparation. $AlPO_4$ had a very low reflecting power even at the wave-lengths for which the reflection was greatest, although the surface was one of the brightest obtained. There was one rather irregular maximum in the first region, and a probable one beyond 20μ. $BiPO_4$, on the other hand, has high and complex maxima in both regions.

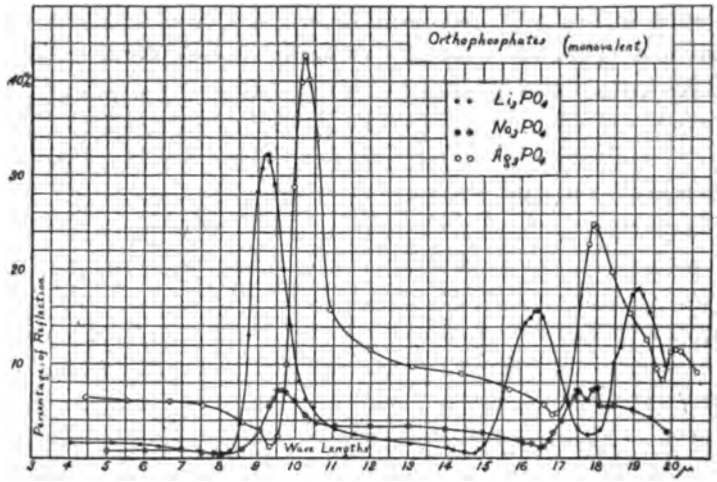

Fig. 3.

It has not been possible with the data obtained to find any distinctive characteristics in the reflection curves which may be ascribed to the chemical group to which the base belongs. Neither have any simple hypotheses suggested themselves which are adequate to interpret the effect of the valence of the base on the complexity of the curves. There seems, however, to be a tendency for the curves to become more complex as the valence of the base increases.

META-PHOSPHATES.

The two meta-phosphates examined, $NaPO_3$ and KPO_3, have monovalent bases. Both curves (Fig. 5) have three reflection maxima between 7μ and 12μ, the middle one being the lowest. $NaPO_3$ was examined to

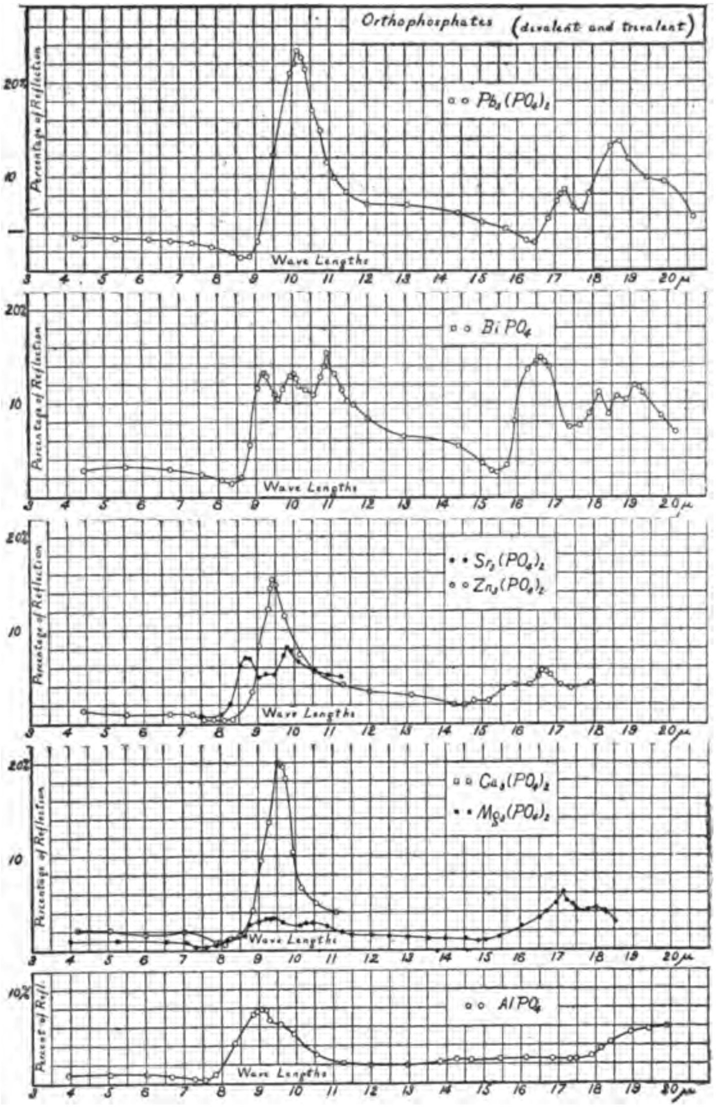

Fig. 4.

20μ and shows a single maximum at 19μ. KPO_3 shows resonance for radiation of greater frequency than does $NaPO_3$ though K has an atomic weight of 39 and Na only 23. Thus an increase in atomic weight of the base is accompanied by a decrease of the wave-length, for which the reflection is a maximum, instead of an increase, as is usually the case. Several different forms of sodium meta-phosphate are known, however, having the formulas $NaPO_3$, $Na_2P_2O_6$, etc., so the sodium meta-phosphate and the potassium meta-phosphate examined might not have been similar. The $NaPO_3$ was amorphous or glassy, and KPO_3 crystalline. The first maximum for $NaPO_3$ at 7.9μ lies close to that found by Coblentz at 8.0μ.

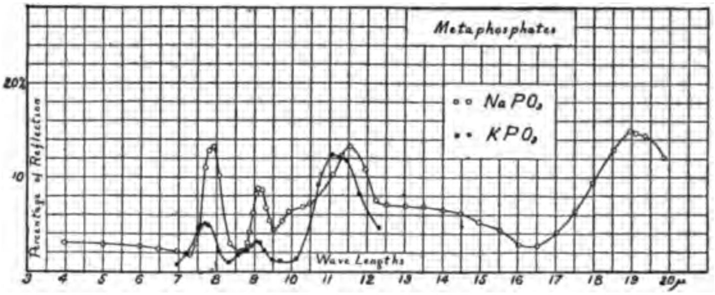

Fig. 5.

Pyro-Phosphates.

Four pyro-phosphates were examined, three with monovalent bases, $Na_4P_2O_7$, $K_4P_2O_7$, $Ag_4P_2O_7$, and one with divalent base, $Pb_2P_2O_7$. A distinguishing feature of these curves (Fig. 6) is that they have no region of low or continuously decreasing reflection between 12μ and 15μ as do all the other phosphates examined. Instead, the pyro-phosphates

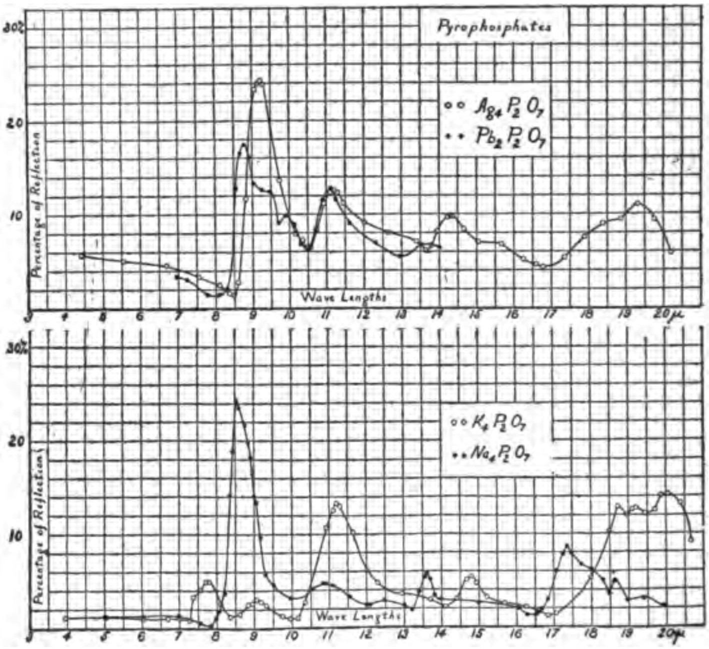

Fig. 6.

have in this region one or two points of pronounced selective reflection. The highest points in the $K_4P_2O_7$ curve are at longer waves than the apparently corresponding ones for $Na_4P_2O_7$ with the lighter base, but if all the maxima are taken in regular order without regard to height, the difference is in the opposite sense. There is a somewhat similar correspondence between $Pb_2P_2O_7$ and $Ag_4P_2O_7$; but the two sets cannot be reduced to one depending on the effect of the weights of the bases.

Little more can be said than that these salts with more complex chemical formulas have more free periods of vibration to which they respond than do the simpler molecules. The table is given to assist the reader in locating the more important maxima. The values of the wave-lengths in the last column are taken directly from the curves.

TABLE.

I., Ortho-phosphates; II., Meta-phosphates; III., Pyro-phosphates.

	Chemical Formula of Salt.	Valence of Base.	Atomic Weight of Base.	Weight of Base Combined with One At. Wt. of P.	Wave-lengths of Reflection Maxima.
I.	Li_3PO_4	1	7	21	9.25, 16.4–19.1
	$AlPO_4$	3	27	27	9.1, (20)
	$Mg_3(PO_4)_2$	2	24	36	9.4, 10.5,17.1
	$Ca_3(PO_4)_2$	2	40	60	9.5,
	Na_3PO_4	1	23	69	9.6, 17.5–18.0
	$Zn_3(PO_4)_2$	2	65	98	9.4, 16.6
	$Sr_3(PO_4)_2$	2	87	130	8.7–9.8
	Bi_3PO_4	3	207	207	9.2–10.0, 16.6–18.15 10.9, 18.60–19.15
	$Pb_3(PO_4)_2$	2	206	309	10.15, 17.25–18.7
	Ag_3PO_4	1	108	324	10.25, 17.9–20.1
II.	$NaPO_3$	1	23	23	7.9–9.15–11.6, 19.0
	KPO_3	1	39	39	7.7–9.1–11.1
III.	$Na_4P_2O_7$	1	23	46	8.5–10.9, 12.5–13.6, 17.4–18.7
	$K_4P_2O_7$	1	39	78	7.75–9.05, 11.2–14.8,
	$Pb_4P_2{}'_7$				18.7–19.15, 20.0
	$Pb_2P_2O_7$	2	206	206	8.–89.5,9.9–11.1, 13.5
	$Ag_4P_2O_7$	1	108	216	9.2–11.2, 14.3–19.3

Fig. 7 shows the position of the most prominent reflection maxima for the ortho-phosphates plotted with wave-lengths as abscissas and as ordinates the weights of the bases united with one atomic weight of phosphorus. To show the magnitude of the deviations from exact proportionality between the wave-lengths and weights of the bases, a straight line has been drawn through the Li_3PO_4 and Ag_3PO_4 maxima in the first region. It is seen from this figure that the deviations do not bear any constant relation to the valence of the base. In the second region two lines have been drawn which include between them all except one of the principal maxima. This region of selective reflection is nearly 3μ broad

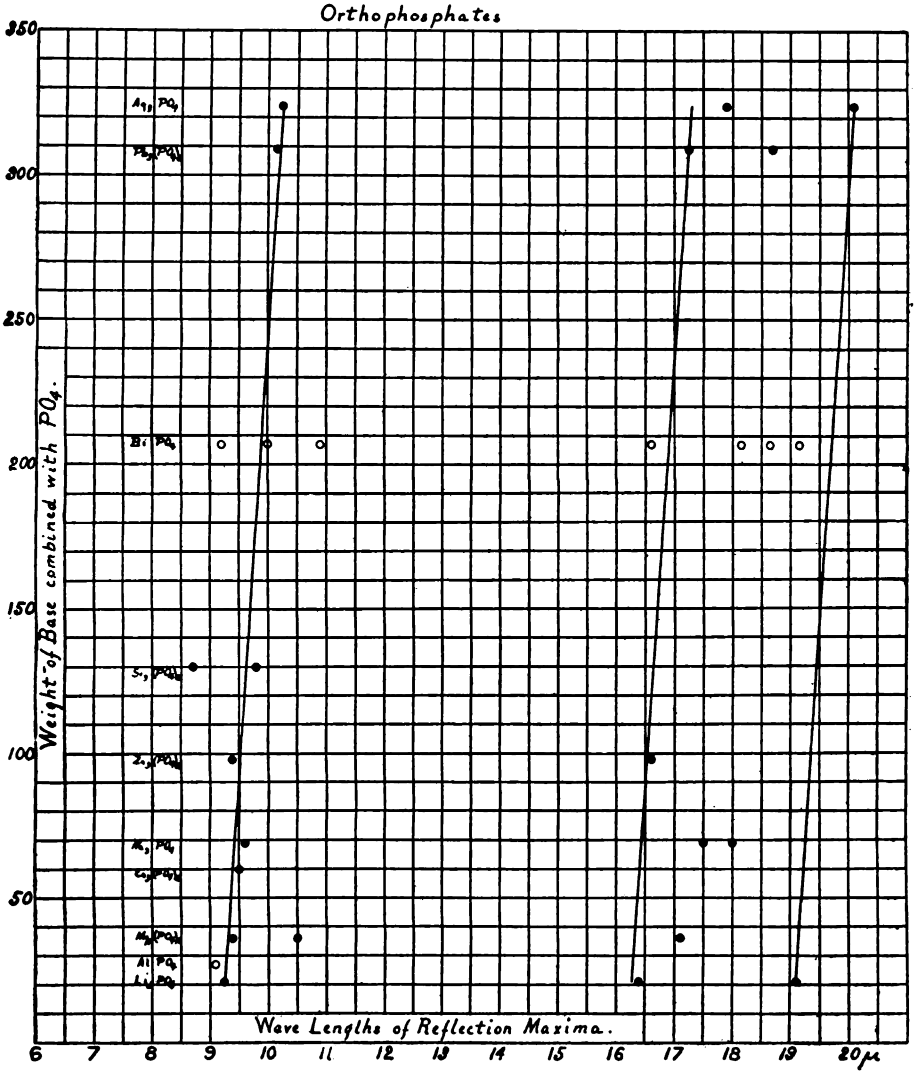

Fig. 7.

and shows a general shift to the long waves with increasing weight of base, though no correspondence between individual maxima can be traced.

It has been shown that[1] a change in the atomic weight of the element combined with oxygen in the acid radical seems to have a greater effect on the position of the reflection band than an equal change in the atomic weight of the base. A comparison of the curves for phosphates with those for sulphates[1] shows that in all cases the first region bands for the ortho-phosphates are at longer wave-lengths, on an average fully .7μ, than those for the corresponding sulphates. This difference cannot be attributed to a difference only in the atomic weights of phosphorus and sulphur for the two have approximately the same weights, that for sulphur being slightly larger (S = 32.0, P = 31.0). Neither does it seem that a difference in the weights of the bases can account for more than a small part of the difference in wave-lengths selectively reflected. This is certainly true if we may for example assume that K_2 and K_3 in K_2SO_4 and K_3PO_4 act similarly to bases of atomic weights 2 × 39 and 3 × 39 respectively. If we should assume that oxygen is the determining element and that the position of the reflection maxima is due to the loading of the oxygen atom with atoms in combination with it, it might be inferred that not only would the precise position be affected by the weight of the base and the acid forming element, but also that the strength of the bonds and the arrangements of the atoms in the molecule would have some influence. Phosphorus has a much stronger affinity for oxygen than has sulphur, for the oxides of phosphorus are decomposed with greater difficulty. What relation this bears to the selective reflection of the solid salts it is impossible to determine with present data.

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[1] Astrophysical Journal, 26, p. 240, 1907.

Merritt[2] and Königsburger[3] both found that between .1μ and 5.5μ the absorption in doubly refracting media depended upon the plane of polarization of the incident energy. Later it was observed that the reflection maxima of calcite and aragonite[4] in the 11μ region differed by .24μ though both calcite and aragonite had the same chemical formula, $CaCO_3$. There were also decided differences in the heights of the reflection maxima, which could not be attributed to a difference in polish. This showed conclusively that the crystal form as well as the chemical composition must be taken into account even when dealing with radiations of wave-lengths over 10μ. More recently the dependence of the selective reflection on both the crystal form and the orientation of the section examined has been very carefully studied by Nyswander[5] in the case of calcite and aragonite using polarized light.

In order to obtain a complete analysis of the dependence of free resonance periods upon the chemical composition of a salt it will be necessary to examine the substance in crystal form and with polarized light. It is, as has already been stated, impossible to find suitable crystal sections of an extended series of salts which have the desired variations in chemical composition. While pressed surfaces cannot give the absolute values of reflection, the minute crystalline structures when present must have all possible orientations and therefore all the free resonance periods of sufficient strength must appear in the resulting curves. A comparison of the relative heights of the reflection maxima observed with pressed surfaces is certainly more trustworthy than such a comparison when crystal sections cut at random are used. For example, the almost complete disappearance of the second region maximum in the witherite examined by Morse[1] is undoubtedly due to the chance orientation of the crystal section. The use of pressed surfaces makes possible the examination of a great number of large and complicated series of salts like the phosphates here described. And the data thus obtained promise eventually to be of much value in selecting the crystal sections best suited to a more complete investigation of the problem.

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[1] Investigations of Infra-red Spectra, Parts IV. and VI.

[2] Phys. Rev., 2, 424, 1895.

[3] Ann. der Phys., 61, 687, 1897.

[4] Astrophysical Journal, 11., 225, 1907.

[5] Phys. Rev., 28, 4, p. 291, 1909.

The main results here presented may be summarized as follows:

1. A surface suitable for the qualitative study of selective reflection in the infra-red spectrum may be produced on a substance which is available only in the form of fine powder, if this powder is subjected to great pressure.

2. The method of making the pressed surfaces described has made it possible to compare the reflection in the infra-red spectrum of extended series of salts, such as phosphates, chromates or chlorates in which a common acid forming element is combined with different weights of oxygen. Data on the selective reflection of phosphates are here given.

3. A comparison of Figs. 3 and 4 for ortho-phosphates with Fig. 5 for meta-phosphates and Fig. 6 for pyro-phosphates shows that each group has a more or less characteristic selective reflection which easily distinguishes it from the other groups of phosphates as well as from salts of other acids, carbonates, nitrates, and sulphates.

4. The data on phosphates alone are an insufficient basis for the formulation of any exact relation between the valence of the base, or the chemical group to which it belongs, and the selective reflection characteristic of the salts of a given acid radical. But in general an increase in the weight of the base combined with the given acid radical containing phosphorus causes the reflection maxima to be moved toward the longer waves, as has been found with salts of other acids.

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[1] Astrophysical Journal, 26, p. 240, 1907.

5. A comparison of sulphates and phosphates shows that phosphorus has a greater effect on the free resonance periods than sulphur for some reason not connected with the relative atomic weights since the reflection maxima occur for longer waves in the phosphates, although phosphorus and sulphur for the rough purposes in hand have practically the same atomic weight.

In conclusion the writer wishes to thank Mr. B. L. Murray, of Merck and Company, for aid in the selection of the phosphates used. She also wishes to thank Dr. L. B. Morse for his interest and assistance throughout the work. And she especially wishes to acknowledge her great indebtedness to Dr. E. F. Nichols who suggested the investigation, and under whose direction is was carried out.

PHŒNIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY, New York,
May, 1911.

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Aerial Locomotion. By E. H. Harper and A. Ferguson. London: Cambridge University Press, 1911. Pp. xii+164.

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THE

PHYSICAL REVIEW.

THE TERMINAL VELOCITY OF FALL OF SMALL SPHERES IN AIR AT REDUCED PRESSURES.

By L. W. McKeehan.

§ I. Introduction.

THE terminal velocity of a freely falling sphere, when all other resistances are negligible compared to that due to the viscosity of the fluid through which the sphere falls, and when no slipping is supposed to occur at the surface of separation, is, as derived by Stokes,[1]

$$V = \frac{\frac{2}{9}ga^2(\sigma - \rho)}{\mu}.$$

In this expression μ is the coefficient of viscosity of the fluid, a the radius of the sphere, V the velocity of fall, g the acceleration of gravity, σ the density of the sphere, and ρ that of the fluid. The exclusion of all but viscous resistance restricts the applicability of the formula to very minute spheres, the condition to be fulfilled being that the radius of the sphere must be small compared to $\mu/V\rho$.

Experimental work at atmospheric pressure by Professor John Zeleny and the writer[2] has shown this formula to hold for spheres of wax ranging in radius from .002 cm. to .00035 cm., spheres of paraffin from .002 cm. to .0005 cm., and spheres of mercury from .001 cm. to .00016 cm., although the measurements on the last named are less accurate than for the other materials, owing to the high reflecting power of their surfaces.

In earlier experiments[3] using natural spores as approximating small spheres, large deviations from the formula given by Stokes were observed, all the spores going too slowly to agree with the formula. It was suggested by Sir Joseph Larmor at the Winnipeg Meeting of the British Association for the Advancement of Science, August, 1909, that experiments at lower pressures would serve to decide whether or not these deviations were due to the formation of eddies in the air near the not perfectly spherical spores. The force required to maintain these eddies would decrease with the density of the gas, whereas the purely viscous resistance should remain constant, since μ is independent of pressure, at least throughout a very great range.[1] If the large deviations observed with spores were due to this cause, the terminal velocity of fall at a lower pressure should be larger than at atmospheric pressure, and should tend to agree more closely with that given by the formula of Stokes.

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[1] G. G. Stokes, Mathematical and Physical Papers, Vol. III., p. 59.

[2] Phys. Rev., Vol. XXX., p. 535; Phys. Zeitschr., Bd. 11, s. 78.

[3] Loc. cit.

Some experiments at low pressures, using lycopodium spores, were performed. These showed, indeed, an increase in terminal velocity, but one of far too great an amount to be due to the suspected cause, since the velocity became at low pressures several times as great as that calculated by the formula. Similar experiments were then performed with perfect spheres of wax, which satisfy Stokes's formula at atmospheric pressure. These showed likewise a large increase in terminal velocity with reduction of pressure, the data so obtained forming the experimental part of the paper here presented. This failure of Stokes's formula at low pressures is traceable to the omission of slip in his derivation. Such slipping of the gas along the surface of the sphere is easily shown to be inseparable from motion in a discontinuous medium, and becomes more important with reduction of pressure as the mean distance between the molecules increases.

The necessity of slip can be seen from the following considerations. The surface layer of molecules in a gas which is moving along a solid surface may be divided into two groups. The first group consists of those which have not yet struck the surface. Their mean velocity will have the component parallel to the surface of the more distant layer of gas from which they come. The second group consists of those molecules which have already struck. Their mean velocity will have a component parallel to the surface smaller than that of the first group, but greater than zero unless the impacts are entirely inelastic. In any case the mean velocity of both groups taken together, which is that of the gas layer as a whole, will have a tangential component, or, in other words, there will be slip between the gas and the solid surface.

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[1] Weinstein, Thermodynamik und Kinetik der Körper, Bd. I., s. 325.

§ II. Theory.

A theoretical discussion of the case was given by Professor E. Cunningham[1] in a paper "On the Velocity of Steady Fall of Spherical Particles through Fluid Medium," which was communicated to the Royal Society of London in January, 1910, by Sir Joseph Larmor. He obtains as the general expression for the terminal velocity of fall of a small sphere in a gas

$$V = V_s\left(1 + A\frac{l}{a}\right),$$

in which V_s is the velocity given by Stokes's formula, l is the mean free path of the gas molecule, a the radius of the sphere, and A a constant whose numerical value depends on the assumption which is made regarding the impacts of the gas molecules on the surface of the sphere. An examination of the results there obtained has revealed some inaccuracies. When these are corrected different values of A than those he obtained are derived.

Suppose in the first instance that the collisions are of the nature of impacts of smooth elastic spheres; the value of A is then 1.5.[2] Suppose next that each impinging molecule enters the surface layer of the particle (whether the solid material or a layer of condensed gas is for the present purpose immaterial), and emerges again from the same area on which it impinged, but with a velocity independent in direction of the relative velocity of the sphere and the molecule before the collision, although of the same mean squared value; the value of A is then 1.2. Suppose that a fraction f of the impacts are of the former type and the rest of the latter; the value of A is then $1.5\frac{4}{5-f}$. These cover the cases treated by Cunningham, who obtained in the combined case $A = 1.63\frac{1}{2-f}$.

As an additional and limiting case suppose that after striking the surface of a particle a molecule of the gas is only able to leave it again when moving in the direction of the normal to the surface; the value of A is then 1.05.

Since the mean free path l of the gas molecule is inversely proportional to the pressure p of the gas, an alternative formula

$$V = V_s(1 + B/ap)$$

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[1] Proc. Roy. Soc., Vol. 83 A, p. 357, February, 1910.

[2] One of the substitutions was made incorrectly in a note published in the Physical Review, Vol. XXXII., p. 341, March, 1911, so that the numerical value of the constant multiplier of l/a is there given wrongly. This mistake was pointed out by Professor R. A. Millikan, who kindly read a part of the analysis leading to the results here given.

can be used, and is more convenient for experimental verification. Calculating the value of B from that of A, using $\mu = 1833 \times 10^{-7}$[1] at 20° C., we get when p is expressed in millimeters of mercury, for

$A = 1.0$ $B = .0075$
1.05 .0078
1.2 .0090
1.5 .0112

The terminal velocity of fall of small spheres should thus increase enormously at very low pressures, and should then become proportional to the radius of the sphere, and not to the square of the radius as at higher pressures. It should also be inversely proportional to the pressure. In Figs. 1 and 2 are plotted as abscissa the reciprocal of the computed velocity, that is, the time required to fall one centimeter at this velocity, and as ordinate the pressure in mm. of mercury. The temperature assumed is 20° C., and the value of the constant chosen is $A = 1.0$, since, as shown later, this is the value obtained by experiment. Six curves are drawn in Fig. 1 for different values of the radius, the value for each curve being given in cm. × 10^{-4} in the upper margin. Fig. 2 shows on a much larger scale the part near the origin omitted from Fig. 1. The close approach to a linear variation of time of fall with pressure should here be noted. It is found upon computation that the criterion for steady motion given above is fulfilled by all the sizes shown at all the pressures.

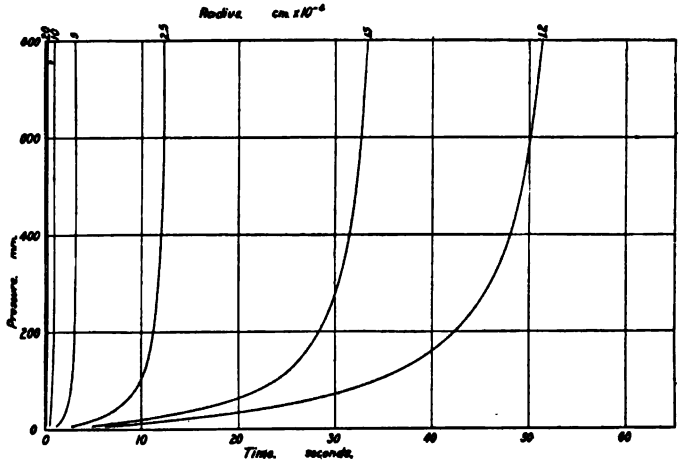

Fig. 1.

The assumption is made that μ has the same value at all pressures. This is required by the kinetic theory of gases and it seems likely that the values of μ obtained experimentally at low pressures are somewhat lower than at atmospheric pressure only because slip is neglected. For this reason the pressure at which μ shows a marked decrease depends on the method used in determining it, and upon the dimensions of the apparatus employed.

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[1] R. A. Millikan, Phil. Mag., VI., Vol. 19, p. 215, February, 1910, $\mu = 1863 \times 10^{-7}$ at 26° C.

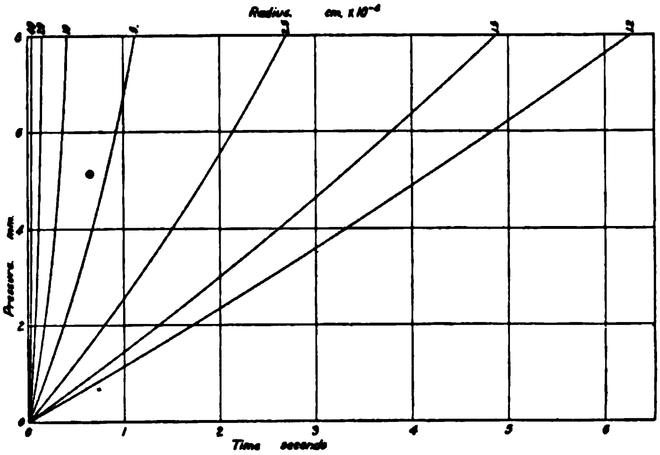

Fig. 2.

§ III. Experiments.

1. *Preparation of Material.*—Minute spheres of wax were made by an atomizer,[1] and were collected by allowing the cloud of spheres so formed to settle on sheets of paper in a closed space about 40 × 40 × 60 cm. The range of sizes obtained could be varied within certain limits by regulating the size and openings of the atomizer, and by varying the temperature of the wax.

2. *Measurements.*—In order to find the value of B in the formula

$$V = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\mu}\left(1 + \frac{B}{ap}\right),$$

the values of σ, the density of a sphere, a its radius, V its terminal velocity of fall, and p the pressure of the gas in millimeters of mercury, were determined for over six hundred spheres of wax.

3. *Density.*—The density σ of the wax was 1.058, as previously determined.[2]

4. *Terminal Velocity of Fall.*—The method of getting the terminal velocity of fall V was the same as that used in the previous experiments,

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[1] The same method was used in the earlier experiments cited. Microphotographs of these perfect spheres are there shown.

[2] Loc. cit.

and consisted in measuring the total time required to fall a known distance of about 31 cm.

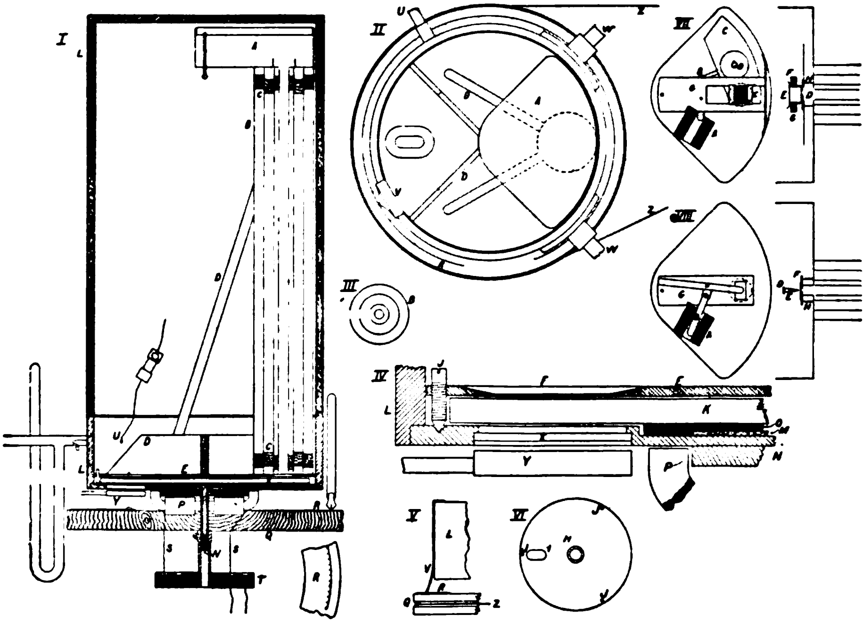

Fig. 3.

Referring to Fig. 3: drawing *I* is a vertical section through the apparatus; *II* is a plan of the same with the cover removed; *III* is a horizontal section through the tube in which the spheres fell; *IV* is an enlarged view of the lower left-hand corner of *I*; *V* and *VI* are details of parts not shown elsewhere; *VII* and *VIII* are plans and sections of two mechanisms used for releasing spheres. The lettering of corresponding parts is the same in the first six drawings.

The spheres released in the fall box *A* fell through the fall tube *B* to the revolving disc *K*. In releasing spheres by the method shown in drawing *VII*, a quantity of them several mm^3. in volume was placed in the cloth-bottomed trough *E*, which slipped tightly into a slot in the frame *G*. A solenoid *A* drew in the soft-iron armature *B*, and by it moved the sliding plate *C* across the short open tube *H* soldered to the bottom of the fall box just under *E*. The sliding plate carried a flexible pointed spring *D* projecting above a small hole in its center. The motion of *C* was stopped by a peg, not shown, when *D* reached the middle of the bottom of the trough *E*, against which it scratched lightly. The vibration produced by this scratch sifted some spheres through the cloth and they then fell through the small hole in *C*, through *H*, and into the fall tube *B*.

In the method shown in drawing *VIII* the spheres were left on the paper upon which they had been deposited after atomizing. A piece of this was put at *F*, with the sphere-coated side underneath, just over a small hole in the frame *G*, which fit tightly in the tube *H*. The solenoid *A*, by means of the armature *B* drew a brass block *C* from beneath a long metal strip *D*, which sprung downward, rapping the point *E* against the upper surface of the paper just over the hole in *G*. The blow was not sufficient to puncture the paper, but it set some of the spheres free and they then fell through *H* into the fall tube.

In the fall tube *B* the spheres, released by either of the methods described, fell through the innermost of four concentric brass tubes, designed to prevent air currents. The outer tubes were pierced at one point, as shown in drawing *III*, to facilitate changes of pressure in the spaces between the wooden rings placed near the ends. The three inner tubes were entirely supported by these rings and were not in contact with any other metal parts. The apparatus was used in a room with double walls and no windows, which provided an excellently steady temperature.

The outer tube was soldered at the top of the fall box *A*, and at the bottom to braces *D*, *D*, and to the brass plate *E*. This plate was supported on three leveling screws *J* (drawing *IV*), one of which rested in a socket, fixing the relative angular position of the fall tube and the outer case *L*. The plate was pierced by two holes, one a narrow radial slot just under the fall tube, and the other a window, 180° from the slot, for viewing the spheres after they had fallen. A plate *H* (drawing *VI*) similar to *E*, but without any fall tube, was substituted for it when measuring the spheres. This provided more room for the measuring microscope.

The surface for receiving the spheres was that of a plate glass disc *K* cemented to a circular brass plate *M*, and rotated under the plate *E* on a pivot in the bearing *N*. On a diameter of the plate *M* was imbedded a soft-iron armature *O* with thickened ends. The poles of this armature were directly over the poles of an electromagnet *P* carried on a wooden wheel *Q*, which was rotated about *N* by a chronograph motor through a belt *Z*. The current for *P* was supplied through wires *S*, *S*, dipping into circular troughs of mercury in the ebonite block *T*. By this device the bearing for the plate *K* was nowhere exposed to atmospheric pressure and required no packing.

At the instant of releasing the spheres the wheel *Q* was set in steady rotation by putting it in gear with the chronograph motor, and as the spheres arrived successively at the bottom of the fall tube they were received at different angular positions on the surface of the plate K. A chronograph pen connected in series with a seconds pendulum, rested on a paper strip R attached to Q, and marked each second as the wheel rotated. This time record is shown in plan just to the right of T, and also in drawing II for a different speed of rotation. After completing the experiment and stopping the rotation of Q, an index V, which fit over the edge of the case L was placed exactly 180° from the place the pen had ceased to mark. When this index pointed to any mark on the pen record as Q was rotated, the spheres which had fallen on K just as that mark was being made would be 180° from the bottom of the fall tube; that is they would be in a position to be seen through the window at F. By counting seconds from the beginning of the pen record to the index the elapsed time of fall was given directly.

This is a longer time than that which would be required if the sphere had started to fall with its terminal velocity, instead of starting from rest. The correction to be applied can easily be found. The following table gives its value for the apparatus used.

Observed Time. Seconds.	Correction. Seconds.
.50	–.06
1.00	–.03
2.00	–.02
3.00	–.01
6.00	–.01
7.00	0

These corrections have been applied to all times of fall less than seven seconds.

5. *Radius of Spheres.*—The radius a of each sphere was determined by measuring its diameter from two to eight times, the majority of the spheres being measured six times. An improved microscope plate micrometer[1] was used except in experiments II., 1, 2 and 3, and for fourteen spheres in other experiments which were too large to be measured by the plate micrometer used. These excepted spheres were measured by an ocular micrometer. The micrometer field was illuminated by diffused light reflected from the mirror Y (drawing IV, Fig. 3), through the window X and disc K. Test measurements using different magnifying powers gave concordant results for all the sizes used, and it appears that the measurements of radii, even for the smallest spheres, are not affected by constant errors due to diffraction, of an amount exceeding a small fraction of a wave-length of light. Some difficulty in the measurement of the smaller spheres was experienced on account of tremors of the

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[1] John Zeleny and L. W. McKeehan, PHYS. REV., Vol. XXXII., p. 530.

pier on which the apparatus stood. The trouble was eliminated by measuring diameters after midnight, when heavy traffic on the streets had ceased. The method of making exterior contact of the cross-hair and the circular image of a sphere was found the most convenient for rapid measurement. A correction for the width of the cross-hair had therefore to be applied to all diameters measured. The amount of this correction was determined by using other forms of contact for comparison. with other objects than spheres.

6. *Pressure.*—The pressure inside the case *L*, which was of brass about 5 mm. thick, was reduced by a water pump or by a Gaede mercury pump, depending upon the reduction desired. The pumps were attached at *U* (Fig. 3). The window *X* was of plate glass set in paraffin which made a permanently air-tight joint. The cover of the case *L* was ground with emery to fit against the lower part, and a thin coating of vacuum wax between the surfaces gave an excellent joint. A platinum wire for the electrical connection to the solenoid in the fall box was sealed through the glass manometer tube outside the case, the return circuit being through the metal parts of the apparatus and its supports *W*, *W*.

Pressure readings were taken by means of a cathetometer on a closed-arm mercury manometer, and when the pressure was low enough it was also measured by a McLeod gauge with a small factor. Glass stopcocks served to isolate the apparatus from the pumps. The apparatus was left to itself for at least three hours just preceding the releasing of the spheres, so that the pressure and temperature of all its parts was steady. A dish containing P_2O_5 was placed inside the apparatus before reducing the pressure. The drying agent was considered necessary, although experiments at atmospheric pressure showed the difference in viscosity due to a small amount of water vapor was not appreciable. At low pressures the same amount of vapor, forming a larger fraction of the whole gas, might change the viscosity considerably, since its viscosity is much less than that of air.

7. *Method of Finding and Measuring Spheres.*—In finding and measuring the spheres the microscope was placed in guides which permitted it to move only along a radius of the plate *K*, 180° from that passing under the fall tube. The distance from the center of the plate was controlled by a slow motion screw. With the microscope focused on the surface of *K*, the wheel *Q* and plate *K* were very slowly turned by hand through suitable gearing, and the spheres were measured as found. Each sphere was placed near the center of the field by moving the plate or the microscope, and the current for the magnet *P* was interrupted during the measurements in order to prevent creeping of the plate *K*. After sur-

veying the whole of one strip or zone the microscope was moved radially the width of the field, and the process was repeated until enough spheres had been measured to show the variation of time of fall with radius, or until no more could be found. The radii for an experiment were not computed from the plate micrometer readings until all had been measured. The total number of spheres that fell to the plate was not greater than three hundred in any one experiment, so that no effect on the velocity due to mutual action between the spheres occurred.[1]

§ IV. Results of Experiments.

In the tables and curves *I* to *XVI*[2] are given the results of the experiments, arranged in order of decreasing pressure. The quantities tabulated and plotted are the radii in cm. $\times 10^{-4}$, and the reciprocals of the terminal velocities, that is the times in seconds required to fall one centimeter at this velocity. On the curves the radii are ordinates and the times abscissae. A small circle is drawn for each sphere measured.

The method of release shown in drawing *VIII*, Fig. 3, was found the most satisfactory of about seven methods, probably because the paper used closed the top of the fall tube throughout the experiment, and so no air currents set up by the movement of parts of the mechanism in the fall box could disturb the air in the tube. Large spheres did not, however, adhere to the paper and were not obtained by this method.

The results at atmospheric pressure using this method are given in Table and curve *I*, except that the spheres for which the radius exceeds .0013 cm. were obtained by the method shown in drawing *VII*, Fig. 3. The results at atmospheric pressure using other methods of release than the one shown in drawing *VIII* are contained in table and curve *II*. In neither of these tables are any spheres given which fell in the first twentieth of the period of a complete rotation of the plate *K*. The largest spheres are from experiments where the time of a rotation was 20 seconds, the smaller ones from experiments where the time was from 200 to 1200 seconds. The error in time measurements is thus kept small throughout the whole range.

The range of sizes used in all the experiments was from $a = .0025$ cm. to $a = .00012$ cm., and the range of pressures from atmospheric pressure (740 mm.) down to .32 mm. of mercury. The total time of fall for the various sizes and pressures varied from .74 sec. to 1,072 sec.

The value of the constant B in the formula was computed for each sphere in experiments VI., X., XIII. and XV., at pressures of 8.28, 2.11,

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[1] Cunningham, loc. cit.

[2] Some of these are omitted here for the sake of brevity.

0.69 and 0.34 mm. of mercury respectively. The average values of B for the four experiments were .00724, .00724, .00826 and .00729, giving a mean value

$$B = .0075 \pm 2,$$

corresponding to

$$A = 1.00 \pm 3.$$

The close agreement of the first, second, and fourth values is accidental, as seen by considering the probable errors in the experiments. The probable errors in the time of fall are large for the largest spheres, and the probable errors in the radius are several per cent. for the smallest spheres. The probable error in the average value of B for an experiment also depends upon that in the pressure, since this is not reduced in taking the average. The errors in pressure for these four experiments are different, since the manometer was used for the first and second, the McLeod gauge for the third and fourth. If the four values are weighted with reference to these probable errors, the weighted mean is found to be a little higher than the unweighted mean given above. These pressures were chosen for computing B because the change in the time of fall from that found for atmospheric pressure is large, and yet the total time of fall is not too small for accurate measurement, as it would be at still lower pressures.

Values of the time per centimeter were computed using the value of A corresponding to the assumption of normal emergence of the impinging molecules, $A = 1.05$, for each pressure used, and for the following values of the radius:

.004
.0035
.003
.0025
.002
.0017
.0014
.0012
.001
.0008
.0006
.0005
.0004
.0003
.00025
.0002
.00018
.00015
.00014
.00013
.00012

These times are plotted on curves *I*, and *III* to *XVI*, Figs. 5 to 9, as small crosses, and it will be seen that the circles representing observed spheres agree well with a line passing through these crosses.

An idea of the great amount of variation in time of fall will be obtained by referring to curve *I*, Fig. 5. The black dot near the left of the figure represents the time of falling one centimeter for a sphere of radius .00014 cm., at a pressure of 0.32 mm. of mercury. At atmospheric pressure this sphere would fall in a time shown by the last cross at the right of the figure. The value of the term B/ap in the formula varies from .003 for a = .004 cm., p = 740 mm., to 196 for a = .00012 cm., p = .0.32 mm. The agreement of the experiments with the formula throughout the entire range is excellent.

The differences in computed velocities produced by using one or another value of A can be seen by referring to Fig. 4. Three curves are drawn, showing the variation of the time required to fall one centimeter (abscissæ) with the variation of the radius in cm. × 10^{-4} (ordinates), at a pressure of 0.32 mm. of mercury, and at a temperature of 20° C. The curve at the left, and the one connected to it by horizontal lines are drawn for A = 1.5 and A = 1.2, respectively, and correspond to the limiting values possible under Cunningham's assumptions. The curve at the right is drawn for A = 1.05, the value corresponding to the assumption of normal emergence of the impinging molecules. Curve *XVI*, Fig. 9, which shows the experimental results at this pressure, agrees almost exactly with this last curve.

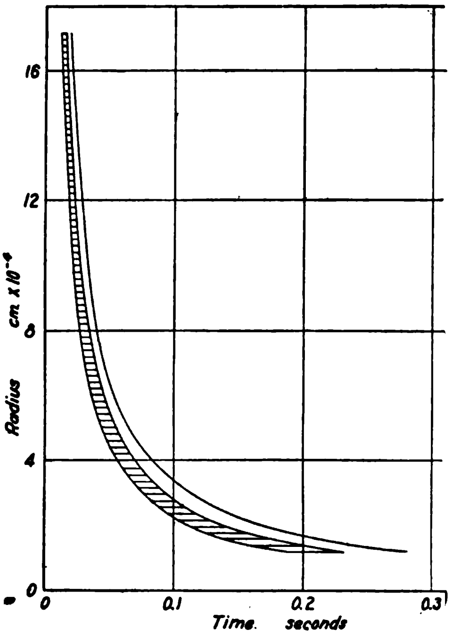

Fig. 4.

At atmospheric pressure the differences are not detectable by the method used, for the range of sizes obtained. This will be seen by comparing curves *I* and *II*, Figs. 5 and 6. The crosses in *II* represent times computed by assuming $A = 0$ (Stokes's formula), those in *I* times computed by assuming $A = 1.05$. The difference amounts to 7 per cent. in time for the smallest sphere shown, being less for all larger spheres, and the additional difference in case $A = 1.5$ would be about 3 per cent., again for the smallest sphere shown. An error of 1.5 per cent. in the measurement of the radius of such a sphere would entirely mask this additional difference in time of fall.

The only other experimental value of the constant in Cunningham's formula is given by Professor R. A. Millikan,[1] who found A to be 0.815. This value is determined from experiments on spheres of different sizes, but all at one pressure, namely atmospheric. The method is indirect in that the radii of the spheres were not measured but were computed from their time of fall on the assumption of uniform electrical charge for all the spheres. The material used was a liquid, and internal eddies in the drops may cause a consumption of energy, and consequently reduce the apparent value of A.

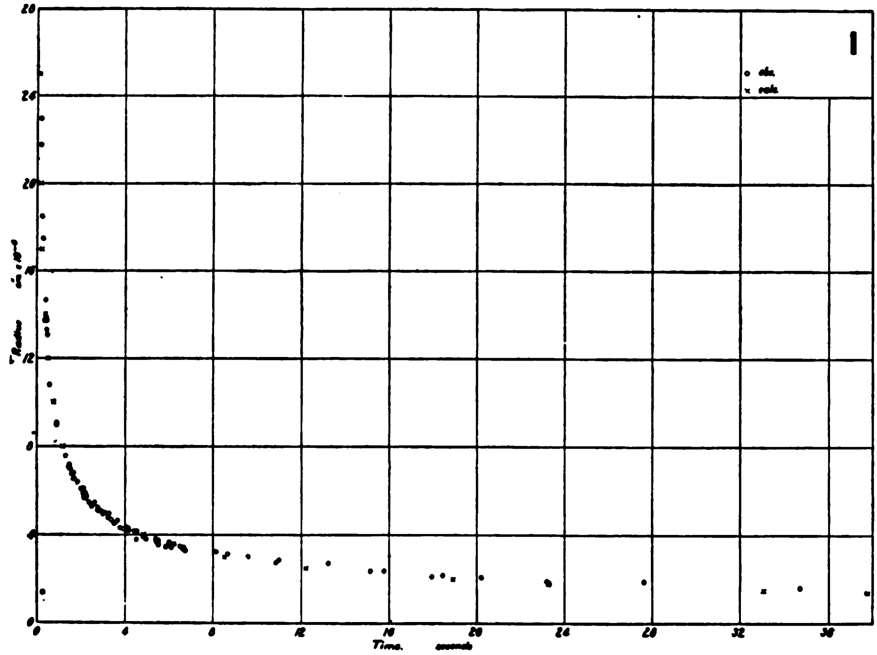

Fig. 5.

Atmospheric pressure.

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[1] Science, Vol. XXXII., p. 446.

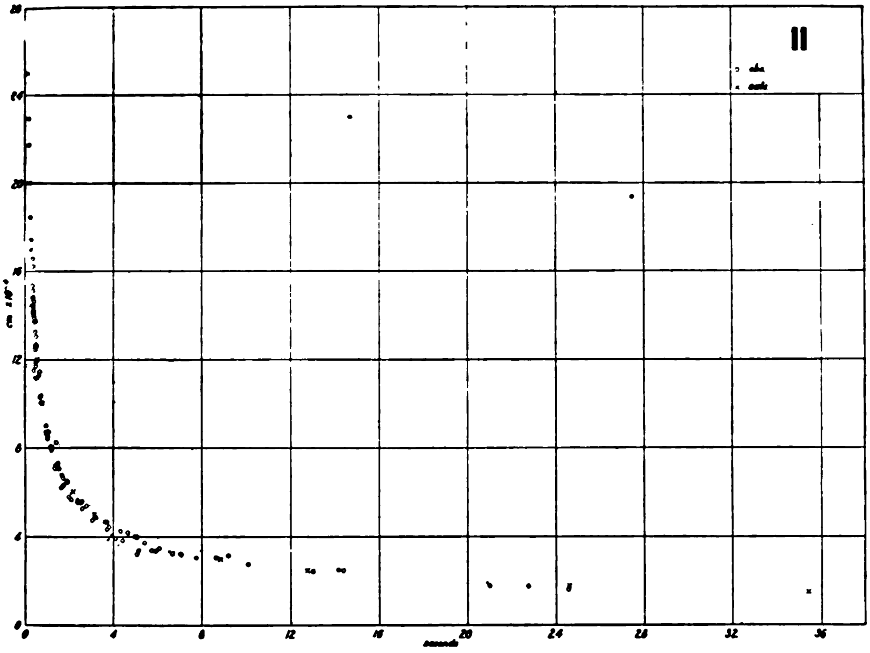

Fig. 6.

Atmospheric pressure.

§ V. Spores.

Lycopodium spores, which fell at atmospheric pressure only about half as fast as Stokes's formula required, were found at lower pressures to maintain the same ratio of observed velocities to velocities computed

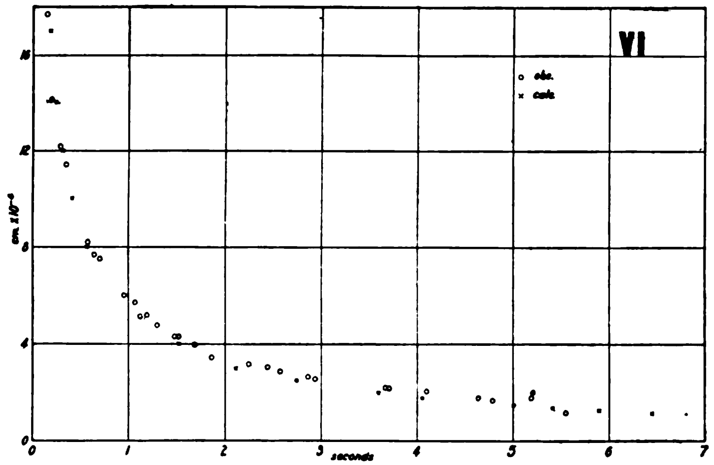

Fig. 7.

Pressure = 8.28 mm.

by the formula which held at all pressures for wax spheres. This means that the density, which is the only measured quantity appearing in the formula in the first degree, was very incorrect. The density determined by refined volumenometer measurements was 1.175. This may have been the density of a solid shell surrounding an air space or the density of a spongy mass containing many air spaces. The average density, meaning by this the quotient of the mass of a spore by the volume of a sphere having its mean radius, would have to be about 0.6 to make the spore behave as it does. In any event, turbulent motion of the air can no longer be held responsible for the variations observed at atmospheric pressure. Experiments with the other spores used before were not attempted, because the condition of the material appeared to have changed with time.

§ VI. Summary and Conclusion.

The formula

$$V = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\mu}\left(1 + A\frac{l}{a}\right),$$

in which A is a constant, expresses the terminal velocity of fall of small solid spheres in air throughout a wide range of radius and pressure. The constant A appearing in this formula is found to have a theoretical value depending on the assumption consistent with the kinetic theory of gases which is made concerning the mode of impact of the gas molecules on the surface of the sphere. Assuming elastic impacts the value of A is 1.5;

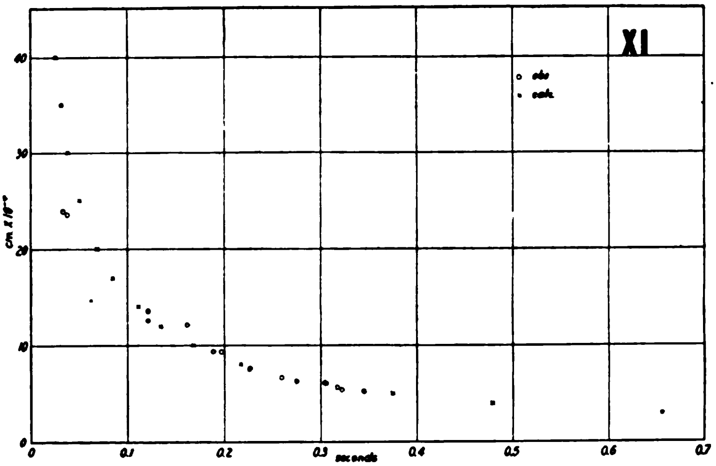

Fig. 8.

Pressure = 2.01 mm.

assuming inelastic impacts and the same distribution of component velocities in the emerging as in the impinging molecules, the value of A is 1.2; assuming inelastic impacts and normal emergence of all impinging molecules, the value of A is 1.05; by experiment the value of A is 1.00 ± 3.

The close agreement of the experiments with the fomula derived for the assumption of normal emergence makes it probable that a gas molecule impinging on a solid is entangled in the surface layer of molecules, and emerges again after a number of collisions with these molecules, its direction of emergence being generally nearly normal to the surface. The experiments do not indicate whether this penetrable layer is composed of the same kind of molecules as the rest of the solid, or is a condensed layer of the gas, but only show that the distances between the molecules in it are small compared to the distances in a gas under normal conditions of temperature and pressure.

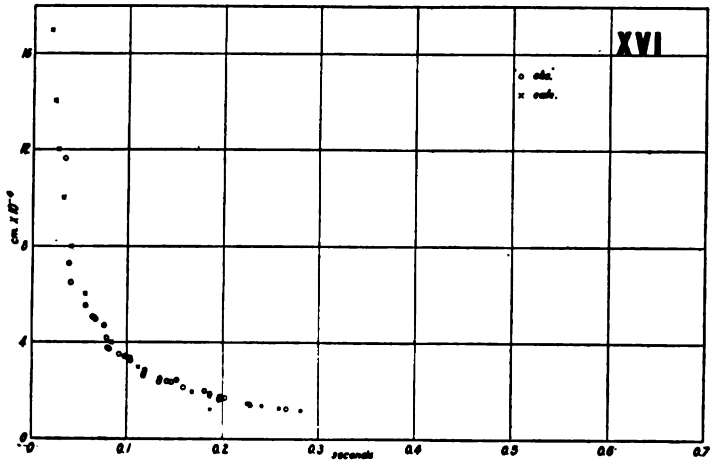

Fig. 9.

Pressure = 0.32 mm.

I take great pleasure in thanking Professor John Zeleny for his continuous interest in the progress of the work, and for his many valuable suggestions on the solution of experimental and theoretical difficulties.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
May 17, 1911.

TABLE I.

Experiment 1. *p* 736 *mm. Temperature* 20°.6 *C. Tube length* 30.9 *cm. Maximum time of fall measurable* 20 *sec.*

a	1/*V*	*a*	1/*V*	*a*	1/*V*
.002293	.1929	.001746	.297	.001369	.481
.002170	.1995	.001461	.419	.001326	.474
.001846	.2404	.001382	.437	.001308	.518

Experiment 2. *p* 749 *mm. Temperature* 18°.3 *C. Tube length* 30.96 *cm. Maximum time of fall measurable* 226 *sec.*

a	1/*V*	*a*	1/*V*	*a*	1/*V*
.001369	.379	.000560	2.296	.000416	4.56
.001077	.600	.000541	2.45	.000407	4.51
.000906	.934	.000541	2.70	.000393	4.86
.000898	.934	.000522	2.56	.000385	4.97
.000757	1.365	.000505	2.86	.000385	5.40
.000719	1.524	.000492	3.36	.000382	4.52
.000696	1.566	.000466	3.47	.000373	5.45
.000679	1.718	.000461	3.75	.000368	5.49
.000674	1.653	.000453	3.65	.000355	5.52
.000653	1.748	.000449	3.59	.000350	5.88
.000637	1.916	.000433	4.10	.000346	6.10
.000608	2.169	.000432	3.86	.000346	6.67
.000604	2.088	.000427	4.18	.000339	6.63
.000585	2.270	.000426	3.96	.000335	6.72
.000580	2.189	.000417	4.18	.000334	6.79

Experiment 3. *p* 740 *mm. Temperature* 19°.7 *C. Tube length* 30.96 *cm. Maximum time of fall measurable* 1,080 *sec.*

a	1/*V*	*a*	1/*V*	*a*	1/*V*
.000704	1.492	.000370	6.03	.000238	15.18
.000571	2.335	.000361	6.26	.000238	15.79
.000562	2.205	.000351	6.52	.000218	18.49
.000518	2.854	.000327	8.17	.000213	17.96
.000502	2.984	.000317	8.69	.000210	20.24
.000490	3.081	.000303	9.63	.000192	23.22
.000473	3.31	.000287	11.03	.000191	27.64
.000413	4.44	.000274	10.86	.000162	34.76
.000378	5.52	.000273	13.26		

TABLE III.

Experiment 1. *p* 100.4 *mm*. *Temperature* 21°.0 *C*. *Tube length* 30.9 *cm*. *Maximum time of fall measurable* 212 *sec*.

a	$1/V$	a	$1/V$	a	$1/V$
.002660	.1462	.001176	.520	.000529	2.52
.002177	.2046	.001068	.695	.000497	2.95
.002069	.2795	.000992	.754	.000497	3.25
.001918	.296	.000833	1.170	.000440	3.49
.001854	.221	.000793	1.011	.000438	3.87
.001840	.260	.000712	1.436	.000320	6.76
.001531	.318	.000641	1.781	.000313	6.60
.001293	.482	.000543	2.64	.000302	6.88
.001207	.497	.000537	2.38		

TABLE IV.

Experiment 2. *p* 34.85 *mm*. *Temperature* 21°.2 *C*. *Tube length* 30.9 *cm*. *Maximum time of fall measurable* 186 *sec*.

a	$1/V$	a	$1/V$	a	$1/V$
.003715	.0715	.001013	.676	.000634	1.501
.002989	.1040	.000975	.669	.000623	1.689
.002642	.1040	.000926	.767	.000532	2.053
.002591	.1234	.000909	.786	.000516	2.339
.001506	.351	.000908	.812	.000487	2.385
.001347	.429	.000808	1.027	.000460	2.781
.001199	.487	.000807	1.053	.000380	4.14
.001109	.604	.000737	1.170	.000331	5.10
.001095	.617	.000635	1.527	.000330	4.71

TABLE VI.

p 8.28 *mm*. *Temperature* 21°.3 *C*. *Tube length* 30.96 *cm*. *Maximum time of fall measurable* 172 *sec*.

a	$1/V$	a	$1/V$	a	$1/V$
.001769	.1427	.000517	1.118	.000263	2.86
.001411	.1978	.000477	1.287	.000257	2.94
.001216	.292	.000430	1.472	.000220	3.67
.001141	.353	.000429	1.517	.000219	3.71
.000819	.584	.000399	1.686	.000204	4.10
.000766	.652	.000343	1.861	.000175	4.64
.000752	.712	.000316	2.250	.000175	5.18
.000599	.960	.000303	2.445	.000169	4.79
.000569	1.067	.000287	2.57	.000119	5.54
.000518	1.183				

TABLE VII.

Experiment 2. *p* 7.70 *mm.* *Temperature* 20°.9 *C.* *Tube length* 30.9 *cm.* *Maximum time of fall measurable* 184 *sec.*

a	$1/V$	a	$1/V$	a	$1/V$
.002090	.1787	.000764	.650	.000466	1.495
.002038	.1787	.000704	.689	.000382	1.589
.001375	.276	.000701	.712	.000327	1.949
.001126	.370	.000688	.731	.000316	1.888
.001065	.491	.000621	.896	.000307	2.066
.001059	.445	.000555	.965	.000306	2.129
.001044	.406	.000525	1.104	.000274	2.556
.000922	.478	.000514	1.072	.000257	2.550
.000916	.500	.000510	1.153	.000210	3.17
.000873	.533	.000507	1.004	.000179	3.12
.000784	.630	.000494	1.134		

TABLE IX.

Experiment 1. *p* 3.14 *mm.* *Temperature* 20°.2 *C.* *Tube length* 30.9 *cm.* *Maximum time of fall measurable* 20 *sec.*

a	$1/V$	a	$1/V$	a	$1/V$
.002042	.0809	.001268	.1832	.000699	.390
.002027	.0923	.001240	.1914	.000687	.419
.002007	.0939	.001145	.1654	.000658	.401
.001966	.1134	.001106	.2012	.000609	.418
.001790	.1150	.001038	.2109	.000565	.460
.001775	.1118	.000930	.2275	.000538	.487
.001372	.1556	.000892	.2616	.000502	.496
.001365	.1540	.000890	.289	.000456	.565
.001327	.1703	.000709	.341	.000321	.625

TABLE XI.

Experiment 1. *p* 2.01 *mm.* *Temperature* 20°.6 *C.* *Tube length* 30.9 *cm.* *Maximum time of fall measurable* 20 *sec.*

a	$1/V$
.002396	.0341
.002358	.0387

Experiment 2. *p* 2.01 *mm.* *Temperature* 20°.5 *C.* *Tube length* 30.9 *cm.* *Maximum time of fall measurable* 19 *sec.*

a	$1/V$	a	$1/V$	a	$1/V$
.001357	.1208	.000768	.2278	.000624	.304
.001213	.1622	.000764	.2274	.000569	.317
.000940	.1888	.000670	.2596	.000515	.322
.000931	.1969	.000626	.275	.000510	.345

Table XII.

p 1.28 *mm.* *Temperature* 20°.7 *C.* *Tube length* 30.9 *cm.* *Maximum time of fall measurable* 18 *sec.*

a	$1/V$	a	$1/V$	a	$1/V$
.002222	.0426	.000808	.1270	.000391	.287
.001616	.0647	.000752	.1494	.000364	.311
.001533	.0672	.000623	.1595	.000340	.348
.001422	.0738	.000588	.1914	.000304	.340
.001323	.0838	.000554	.2034	.000294	.399
.001320	.0844	.000512	.259	.000293	.420
.001164	.0893	.000408	.280	.000281	.392
.001049	.1082	.000401	.324	.000245	.457
.001033	.0910	.000394	.321	.000233	.548
.000883	.1248				

Table XVI.

p 0.32 *mm.* *Temperature* 21°.3 *C.* *Tube length* 30.96 *cm.* *Maximum time of fall measurable* 17 *sec.*

a	$1/V$	a	$1/V$	a	$1/V$
.001163	.0341	.000349	.0992	.000239	.1472
.000730	.0379	.000347	.0973	.000216	.1598
.000647	.0405	.000340	.1028	.000202	.1816
.000548	.0564	.000327	.1031	.000190	.1871
.000501	.0638	.000289	.1177	.000178	.1968
.000494	.0668	.000273	.1167	.000172	.2024
.000468	.0752	.000263	.1161	.000163	.1961
.000415	.0788	.000253	.1346	.000142	.228
.000381	.0798	.000244	.1524	.000127	.266
.000379	.0814	.000242	.1417		
.000357	.0914	.000239	.1333		

HEAT OF EVAPORATION OF WATER.

By Arthur Whitmore Smith.

THE "heat of evaporation" of water means the heat per gram required to change water into saturated vapor at the same temperature. Various determinations of this value have been made during the past century,[1] the most extensive investigation being the work of Regnault[2] over sixty years ago. In the older methods steam from a boiler was passed directly into a calorimeter, where it was condensed. The heat of condensation was measured by the increase in temperature of the cold water of the calorimeter, while the amount of vapor was determined by weighing the condensed water. In more recent experiments the water was boiled in the calorimeter, a known amount of heat being supplied by an electric current. The amount of water thus removed from the calorimeter was determined either by the loss in weight of the containing vessel,[3] or by condensing the steam and weighing the water thus collected.[4]

It is now well known among mechanical engineers that the vapor rising from boiling water carries with it a certain amount of water in a finely divided state, but nevertheless still liquid. The amount of water thus carried in the steam is often over one per cent., and it may be several per cent. of the whole. This leads one to inquire what quality of steam was used in previous experiments to determine the heat of evaporation. If the steam used contained 1 per cent. of moisture it is evident that the familiar number 537 is 1 per cent. too low.

Regnault appears to have known something of the difficulty of obtaining dry steam, and in his classical experiments collected the steam by means of a long tube coiled in the upper part of his boiler. It is now known that this precaution is not sufficient. The later determinations by Joly[5] with a "steam calorimeter," and by Henning vigorously boiling water in a small calorimeter[6] with no separator, certainly were made with steam containing an uncertain amount of moisture.

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[1] See Preston, Theory of Heat, p. 378 ff.

[2] Regnault, Institute de France, Mem. Acad. Sci., Vol. 21, pp. 1–748, 1847.

[3] Griffiths, Phil. Trans., Vol. 186 A, pp. 261–342, 1895.

[4] A. W. Smith, Phys. Rev., Vol. 25, pp. 147–170, 1907. Henning, Ann. der Phys., Vol. 21, pp. 849–878, 1906; Vol. 29, pp. 441–465, 1909.

[5] Joly, Phil. Trans., Vol. 186 A, note on p. 322, 1895.

[6] Henning, loc. cit., Fig. 1, p. 446.

It is the object of this research to determine the heat of evaporation of water at the boiling point more exactly than has yet been done, and especially to eliminate this serious error which apparently has gone unnoticed. The practical need of knowing the exact value of this constant is evident, since it is the basis of the steam tables used in all problems in steam engineering, and a change in this value means a corresponding change throughout the steam tables.

The relative values of the heat of evaporation at different temperatures have been well established by the recent investigation by Davis[1] on the results obtained in experiments on the free expansion of dry steam. Unfortunately the absolute value at any point on his curve is unknown, and steam tables[2] based on this curve assume for the value at 100° C. the mean of the results obtained by Joly and by Henning.

If a reliable determination of the heat of evaporation can be obtained at any one temperature it will have the effect, through this curve, of establishing its value throughout the range of temperatures used in steam engineering.

As far as I am aware, no attempt has ever been made to determine the heat of evaporation from a quiet surface of water. Evaporation from such a smooth surface is supposed to take place by one molecule at a time leaving the liquid and going into the vapor. The action inside of a steam boiler is very different from this, and it would be surprising not to find some fine spray thrown into the steam. It is from this point of view that the problem has now been attacked.

Method.

A gentle stream of dry air is drawn through the calorimeter, passing over the unruffled surface of the hot water and carrying away some of the vapor. Near the boiling point water evaporates very readily, and care must be exercised not to overcool the calorimeter by too rapid evaporation. Heat is supplied by an electric current, and the air current is constantly regulated to allow the evaporation to proceed just fast enough to keep the temperature constant at 98° C. After passing out of the calorimeter most of the vapor is condensed in a cold flask, while the remainder is caught by drawing the air through sulphuric acid. The gain in weight gives the amount of water evaporated in the calorimeter.

The heat received by the calorimeter is that generated in the heating coil plus a small amount which comes from the surroundings by radiation and conduction. The latter cannot be measured directly, but it can be eliminated in the computations by the following method. Each result is computed from two experiments, in one of which a large amount, and in the other a much smaller amount of water is evaporated. The temperatures and other conditions are the same in each and so also is the amount of heat received from the outside. Therefore the difference between the two total amounts of heat eliminates these corrections and is the same as the difference between the two amounts of heat delivered by the current alone. This difference, divided by the difference between the corresponding amounts of water, gives the heat per gram necessary to evaporate water at this temperature.

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[1] Davis, Journ. Am. Soc. Mech. Eng., No. 1212, Vol. —, pp. 1419–1452.

[2] Marks and Davis, Steam Tables, Longmans, 1909.

Thus let M' denote the number of grams of steam produced in a given experiment, H' the corresponding amount of heat supplied by the current, and h the small amount of heat gained by radiation, conduction, etc. Then

$$H' + h = LM', \tag{1}$$

where L is the heat of evaporation. On another day the experiments are repeated under the same conditions as before, but using a larger amount of heat. Then

$$H'' + h = LM'', \tag{2}$$

and combining these two equations by subtraction gives

$$L = \frac{H'' - H'}{M'' - M'}. \tag{3}$$

All corrections for heat gained by radiation or conduction, whether known or unknown, are eliminated by this method of differences. There were no starting or stopping corrections, as each experiment, so called, was a one hour section from the middle of an all day run. The calorimeter, C, and all of its surroundings, shown in Fig. 1, were kept hot, day and night, by the steam-bath. Early in the morning the calorimeter was filled with hot distilled water and maintained at 98° C. all of the forenoon. After noon the heating current was started and the air regulated to hold the temperature constant at the same point. Only after a preliminary run of an hour or so, and when everything was running smoothly and constant, was the steam directed into one of the weighed flasks, and an experiment begun. A second and third experiment might follow, but not more than three runs were made during one day.

Variations.—All of the experiments were made at 98° C., as it was necessary to keep below the boiling point. Since the latter varied from day to day over a range of nearly one degree, the corrections due to heat received by radiation, etc., varied by 100 per cent. Sometimes a series of experiments in each of which a large amount of water was evaporated, were made on one day; and a similar series of check experiments in each of which a small amount of water was evaporated were made on another day when all other conditions were as nearly the same as possible. At other times such check experiments were made at the beginning of the afternoon, and immediately followed by the experiments with larger heats. Again, the check experiments followed the regular experiments. Thus in all respects were the check experiments performed under the same conditions as the others, except in the amounts of water evaporated.

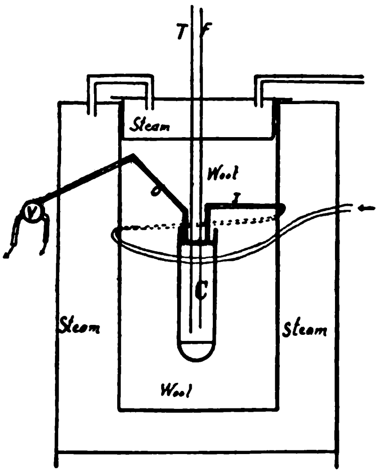

Fig. 1.

Calorimeter and steam jacket.

The Calorimeter.

The calorimeter consists of a thermos bottle, or vacuum walled jar, fitted with a copper lining which serves the double purpose of equalizing the temperature between the top and bottom and enabling the connecting tubes to be soldered in air tight. The internal arrangement is shown in Fig. 2.

The heating coil is made of about one ohm of manganin wire wound on a brass tube, and well insulated with silk and shellac, the whole being enclosed within a larger tube so that no water could come in direct contact with any part of the coil. The leads, *LL'*, were of heavy copper wire to reduce the amount of heat produced in them by the current, and which might then be conducted into the calorimeter. Potential leads, *pp'*, were soldered to the main leads close to the top of the calorimeter.

The glass tube, *F*, for filling and emptying the calorimeter, and the thermometer, *T*, were passed through snug fitting brass tubes which extended well into the water, thus completely sealing the joint. The rotary stirrer drew the water up through the tube on which the heating coil was wound. Friction was very small as it was mounted on glass bearings, and conduction of heat along the stirrer rod, *S*, was reduced to a minimum by making it of wood. The brass tubes, *I* and *O*, for conveying the air current in and out were long and very thin-walled in order that the heat conduction might be as small as possible.

The incoming air was directed downward upon the surface of the water, while the outgoing stream of air and vapor passed through a coil in the water to warm it, if necessary, to the same temperature. Whatever small difference of temperature there may be between the incoming and outgoing air is measured by thermal junctions, *Th*, inserted into the tubes near the top of the calorimeter and corrections made therefor.

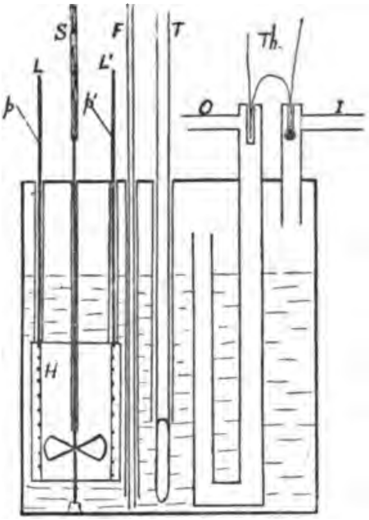

Fig. 2.

Interior of the calorimeter.

THE THERMOMETER.

The temperature of the water in the calorimeter was measured by the thermometer, *T*, which was graduated on the stem to hundredths of a degree, and could be read to thousandths. It was kept in the calorimeter all of the time and thus not subjected to great changes of temperature during the course of these experiments.

The readings of this thermometer do not enter into any computation, and the final result is independent of all temperature measurement. The thermometer serves merely as an indicator to enable the observer to keep the calorimeter at a constant temperature. The only use made of the actual reading is in determining the temperature at which the water was evaporated. The 98 degree mark was chosen as the constant temperature at which to hold the calorimeter. The upper fixed point of the thermometer was carefully determined by means of a regular hypsometer, the test being made in the same room and with the same stem correction as when the thermometer was used. The corrected value for the 98 degree mark was thus determined to be 98.07° C.

ELECTRIC HEATING.

The current for the heating coil was supplied from three sets of storage cells in parallel, and after the first two hours was remarkably steady. often maintaining five amperes without a change in the potentiometer for an hour. Both the current and the fall of potential over the heating coil were measured in terms of a Weston normal cell, and the heat computed from the formula,

$$\text{Heat} = EITJ.$$

The electrical connections are shown in diagram by Fig. 3. The heating coil, *H*, is in series with a standard one-fourth ohm coil, *C*, the storage battery, a variable resistance, *v*, and an ammeter. The current was set at about the desired value and allowed to flow undisturbed. In parallel with *H* are two accurate high resistance boxes, *P* and *Q*. *P* remains set at 10,000 ohms, while *Q* is varied so as to maintain the fall of potential over *P* equal to the E.M.F. of the standard cell, E_s. Then the fall of potential over *H*, being the same as over *P* and *Q* together, is

$$E = \frac{P + Q}{P} E_s.$$

As the constant use of the standard cell would be liable to polarize it, this comparison is made by substitution, the fall of potential over *AB* in the auxiliary circuit *ABr*, being first balanced against th standard cell, using key *K'*, and varying *r*; then this fall of potential is balanced against that over *P*, using key *K* and adjusting *Q*.

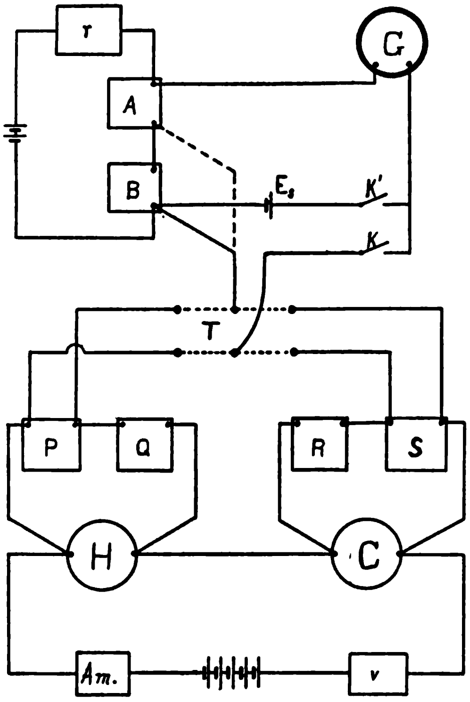

Fig. 3.

Electrical connections.

In the check experiments, where the heating current is only half as large, the cell is balanced against both *A* and *B*, which are 10,000 ohms each, and then the fall of potential over *P* is balanced against that over *A* alone, as shown by the dotted connection.

The current is determined by measuring the fall of potential *E'*, over the standard resistance in the same way, by means of the double throw switch *T*, and its value is computed by the relation,

$$I = \frac{E'}{C} = \frac{R + S}{CS} E_s.$$

The total current is larger than this by the shunt current through R and S; and for the same reason the current through the heating coil is smaller than the total current by the current through the shunt P and Q. These shunt currents are made equal by keeping P and S each set at 10,000 ohms, and thus the current through H is strictly equal to that through C. The resistances enter as ratios of coils in the same box and therefore require no temperature correction. The ratios were calibrated by comparison with standard coils from the Reichsanstalt. The exact values of E, and C were determined by the Bureau of Standards.

Measurement of Time.—Each run was for a period of one hour, this interval being measured by a standard Riefler clock. The connection between clock and calorimeter was made by means of a high grade stop watch with a split seconds hand. Just on the hour by the clock, the time was recorded on the watch by stopping the lower half of the moving seconds hand. One minute later, with the watch held in the left hand and the right hand on the distributing valve, V, of the calorimeter, both hands were turned, one stopping the upper half of the seconds hand at the same time that the other turned the valve. Turning this valve ended one run and began the next. The exact time at which this was done could then be read from the watch to the nearest fifth of a second, and this was usually an even minute after the reading of the clock.

The Mechanical Equivalent of Heat.—The energy delivered to the calorimeter by the current is EIT joules. When it comes to translating this into heat units (calories) it is necessary to use the factor known as the mechanical equivalent of heat. And since the specific heat of water is not constant, but has a different value at each temperature, it is necessary to define precisely what is meant by the term "calorie." The unit used in this paper is the "mean calorie," that is, one per cent. of the heat that is required to warm one gram of pure water from 0° C. to 100° C.

The best direct determination of the mechanical equivalent of heat is doubtless that of Reynolds and Moorby[1] in which they found

$$1 \text{ mean calorie} = 4.1836 \times 10^7 \text{ ergs.}$$[2]

Probably the best determination of this constant by the electrical method is that of Callendar and Barnes[3] who found

$$1 \text{ mean calorie} = 4.1849 \text{ joules,}$$[4]

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[1] Reynolds and Moorby, Phil. Trans., Vol. 190 A, pp. 301–422, 1897.

[2] For a more complete discussion of this subject see paper by A. W. Smith, United States Weather Review, Vol. 35, pp. 458–463.

[3] Callendar and Barnes, Phil. Trans., 1902.

[4] Barnes, Proc. Roy. Soc. Lond., Vol. 82, p. 390, 1909.

provided the E.M.F. of their Clark cells be taken as 1.4333 volts at 15° C. This is equivalent[4] to taking the E.M.F. of the standard Clark cell as 1.4330 at 15° C. or the Weston normal cell as 1.0187 volts at 20° C.

Since January 1, 1911, the E.M.F. of the Weston normal cell is taken as 1.0183 volts at 20° C., and all of my measurements are made in terms of this unit. Therefore, since the electrical determination of J includes E^2, and any reduction in the number expressing the latter will reduce the former twice as much, the value for the mechanical equivalent of heat which should be used in connection with the value of 1.0183 for the Weston normal cell is

$$4.1849 \times \left(\frac{1.0183}{1.0187}\right)^2 = 4.1816.$$

The mean between these two values is 4.1826, and this is the value used in reducing my measurements to mean calories.

Collecting the Water.

The most difficult part of the work was the determination of the amount of water evaporated. While the value of the electric current can be accurately measured at any instant, the only way to find the corresponding rate of steam production is to collect the steam for an hour or so and weigh it. During this period, and for several hours preceding it, the rate of evaporation and the temperature of the calorimeter must be maintained constant, and this means continuous observation of the thermometer and adjustment of the air current. This is tedious, but necessary.

After leaving the calorimeter the stream of air and vapor passes through a two way valve, V, Fig. 1, by which it can be directed into either one of two sets of collecting tubes. In order that there should be no condensation of vapor in this valve or the connecting tubes they were enclosed in a box with an electric lamp which maintained the temperature at 130° C. The steam then passed into a half liter glass flask in a cold water-bath, where most of it was condensed. The remaining vapor, with the air, passed through three tubes containing H_2SO_4 where the water was all caught. (The incoming air was likewise dried by passing through H_2SO_4.) The acid, of density 1.84, was very efficient in collecting the water, practically none of it getting through the first tube. As soon as the second tube began to catch water the first tube was refilled with fresh acid.

Weighing the Tubes.—The tubes and bulbs in which the water was caught were allowed to stand some time to assume room temperature.

They were then carefully wiped with a clean towel and weighed on a sensitive balance. All weighings were made with the aid of counterpoise consisting of a glass tube or bulb as nearly as possible like the one being weighed and likewise containing acid or water, as the case might be. All the tubes were kept closed except when on the balance; then the closing plug was a glass tube nearly sealed off. This allowed the pressure inside the tube to become the same as that outside, which is very important. The weighings were corrected for the buoyancy of the air, and to the weight of water thus determined was added the weight of the vapor filling the space in the calorimeter that had been occupied by the evaporated water.

RESULTS.

The results of these experiments are shown in Table I. Each value is computed from the results of two separate experiments. In the first column is shown the amount of water evaporated during one hour by a current of about five amperes. In the second column is given the amount of water evaporated by about half as large a current during an hour on

TABLE I.

Heat of Evaporation of Water from a Smooth Surface at 98.07° *C.*

Water Evaporated (Grams).			Heat Supplied (Calories).			Calories Per Gram.
Large.	Small.	Difference.	Large.	Small.	Difference.	
37.3531	9.8858	27.4673	20,354	5,340	14,914	542.98
37.7645	9.1421	28.6224	20,379	4,888	15,491	541.23
37.7314	9.1132	28.6182	20,347	4,875	15,472	540.64
37.7146	9.1421	28.5725	20,375	4,888	15,487	542.03
37.5230	9.8858	27.6372	20,328	5,340	14,988	542.32
37.6916	9.8805	27.8111	20,379	5,320	15,059	541.48
37.6609	9.8805	27.7804	20,387	5,320	15,067	542.37
36.7130	9.3242	27.3888	19,816	4,974	14,842	542.15
36.6852	9.3242	27.3610	19,786	4,974	14,812	541.36
36.6826	9.3242	27.3584	19,784	4,974	14,810	541.34
36.5830	9.1421	27.4409	19,786	4,888	14,898	542.91
36.4116	9.1132	27.2984	19,689	4,875	14,814	542.68
36.4976	9.1421	27.3555	19,744	4,888	14,856	543.08
40.2116	8.6613	31.5304	21,686	4,582	17,104	542.12
36.8091	9.3242	27.4849	19,866	4,974	14,892	541.82
36.7000	8.6612	28.0388	19,750	4,582	15,168	540.96
37.3713	9.3242	28.0471	20,166	4,974	15,192	541.66
36.7925	8.9111	27.8814	19,878	4,774	15,104	541.73
36.1450	8.9735	27.1715	19,676	4,955	14,721	541.79
36.0249	8.9735	27.0514	19,612	4,955	14,657	541.83
					Mean	541.93

another day when all the other conditions, as nearly as possible, were the same as on the first day. The difference between these amounts is given in the third column. The corresponding amounts of heat supplied to the calorimeter and their difference, are shown in the three succeeding columns.

The values in the last column are computed from these differences by formula (3), and each one is an independent determination of the heat of evaporation of water at 98.07° C. The mean of these values gives 541.93 mean calories per gram. At 100° C. this would be 1.23 less, or

$$L_{100} = 540.70 \text{ mean calories per gram.}$$

The probable error of this result, computed by the method of least squares from the variations among the individual determinations, is 0.025 per cent.

The work of Davis referred to above leads to the relation,

$$H_t = H_{100} + .3745\,(t - 100) - .000990\,(t - 100)^2,$$

where H_{100} denotes the unknown total heat (above 0° C.) of evaporation at 100° C., and H_t is its value at t° C. We can now write

$$H_t = 640.7 + .3745\,(t - 100) - .000990\,(t - 100)^2,$$

which gives the value of the total heat of evaporation, expressed in mean calories, at any desired temperature t° C.

TABLE II.

Heat of Evaporation of Water when Boiling at 100° C.

Water Evaporated (Grams).			Heat Supplied (Cals).			Calories per Gram.	Temp.	Heat of Evaporation at 100° C.
Large.	Small.	Diff.	Large.	Small.	Diff.			
36.6929	8.9916	27.7013	19,894	4,979	14,915	538.4	99.30	538.0
36.7879	8.9693	27.8186	19,905	4,946	14,959	537.7	99.30	537.3
36.0010	8.4318	27.5692	19,440	4,680	14,760	535.4	99.64	535.2
35.7199	8.4318	27.2881	19,316	4,680	14,636	536.4	99.66	536.2
							Mean	536.7

While this result is about one per cent. larger than the old value, it is not as much larger as might have been expected if we are to believe the current statements that steam often carries several per cent. of moisture. Nor is there much chance of any constant error due to this method, or the apparatus, as a number of experiments were made in precisely the same way as those described above except that the air current was much reduced. This allowed the water to boil, while the air current was only enough to keep the steam moving in the right direction and to prevent its working back and condensing in the incoming air tube. The data from these experiments are shown in Table II., and the final result, reduced to 100° C., gives 536.7 mean calories per gram. This shows that the old value can be obtained with this apparatus by using the old method and allowing the water to boil. By merely checking the boiling and causing the evaporation to take place from the smooth surface of the water the heat of evaporation is increased by 4 calories per gram. This is probably due to the fact that the steam leaving the calorimeter in the latter case is all vapor, while in the former case some liquid is also carried away and counted as vapor.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
May 11, 1911.

THE DISTRIBUTION OF CURRENT AND THE VARIATION OF RESISTANCE IN LINEAR CONDUCTORS OF SQUARE AND RECTANGULAR CROSS-SECTION WHEN CARRYING ALTERNATING CURRENTS OF HIGH FREQUENCY.

BY HIRAM WHEELER EDWARDS.

I. INTRODUCTION.

THE present paper undertakes the investigation of the virtual resistance, inductance and current distribution of long, straight conductors of square and rectangular cross-section, when carrying alternating currents of high frequency. Experimental observations are given, which, within certain limits, corroborate the calculations for virtual resistance, but no attempt was made to measure the current intensity and inductance. Approximate formulas are derived by means of which the virtual resistance, the inductance and the current intensity may be calculated for particular cases.

The problem of determining the virtual resistance and inductance of long, straight, isolated conductors, when carrying alternating current is not a new one. In the oscillating current circuit of wireless telegraph, the increase of resistance due to the high frequencies of alternation is a very impotrant factor. The Tesla experiments illustrating the "skin-effect" show that in a number of cases the virtual resistance is many times the resistance offered to direct current. In the alternating-current railroads, the use of the rails for the return circuit is impracticable because of the increased resistance.[1]

For long, straight, cylindrical wires, Maxwell[2] has developed an expression for the virtual resistance and inductance. Rayleigh[3] has modified Maxwell's results by showing that the permeability of the material of the conductor, if greater than unity, causes a further increase in the resistance. Kelvin[4] solved the problem in a different manner, obtaining results similar, in final form, to those of Maxwell. He has given simplified forms of expression for virtual resistance and inductance for the particular cases of low and high frequency. In a recent paper, Nicholson[1] has published another solution of this problem. He considers first two parallel conductors carrying equal currents in opposite directions and then arrives at the case of the single wire by neglecting the effect of the second upon it. In a paper on the "Effective Resistance and Inductance of a Concentric Main," Russell[2] has given formulas for the virtual resistance and inductance of a concentric main with a solid inner conductor. The expression for the virtual resistance is conveniently arranged so that the resistance of either the core or the sheath may be calculated for any particular case. He shows how the formulas become simplified for the cases of direct current and alternating currents of low and high frequency. A consideration of the current density in the inner and outer conductors of the main is another feature of this paper.

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[1] Standard Handbook, for El. Eng., Sec. 2, No. 122; Sec. 11, No. 33.

[2] Maxwell, E. & M., Vol. 2, third ed., p. 320. See also Gray, E. &. M., Vol. 2, Pt. 1, p. 325; and Thomson, Recent Researches in E. &. M., Chap. 4.

[3] Rayleigh, Phil. Mag., Vol. 21, 1886, p. 381.

[4] Kelvin, Math. & Phys. Papers, Vol. 3, p. 462.

Mordey[3] has employed Kelvin's formulas in the numerical computation of the increase of resistance of a cylindrical conductor, when carrying alternating currents of commercial frequency, 80 to 133 complete cycles per second. Thus with a frequency of 80, the resistance of a copper conductor, 2.5 cm. in diameter, increases 17.5 per cent. The same percentage increase is computated for a conductor of 2.24 cm. at 100 cycles per second, and also for a conductor of 1.036 cm. at 133 cycles per second.

Fleming[4] has measured the ratio of the virtual to the direct current resistance of cylindrical wires using alternating currents of frequency somewhat less than half a million per second. For example, with a frequency of 440,000 using a copper wire, no. 14 standard wire gauge, he finds the ratio to be 5.46 by Russell's formula while his measured value is 5.90. He considers this agreement between the values, which differ by about eight per cent., as satisfactory. Values are given below for cylindrical wires which differ by less than one per cent., and for square and rectangular sectioned wires about four per cent. The experimental work on cylindrical wires, cited below, was performed with slightly damped oscillating currents, to determine whether the damping was great enough to make any appreciable difference between the results observed from damped currents and calculated by a formula derived upon the assumption that the currents were undamped. Fleming used undamped oscillations in obtaining his values.

2. EXPERIMENTAL METHOD.

(*a*) *Production of Currents of High Frequency.*—The two most common methods of producing alternating currents of high frequency are the singing-arc method and by the discharge of a condenser through an inductive resistance. Both methods were tried but greater success was obtained by the latter, so it was adopted in the experimental work herein recorded. The oscillations of current from a condenser are more or less damped, but the damping was reduced to such a magnitude, in the circuits here described, that the results did not appreciably differ from those which would have been obtained from using undamped currents.

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[1] Nicholson, Phil. Mag., Vol. 17, 1909, p. 255.

[2] Russell, Phil. Mag., Vol. 17, 1909, p. 524.

[3] Mordey, Electrician, May 31, 1889, p. 94.

[4] Fleming, Electrician, December 17, 1909, p. 381.

The scheme of connections is given diagramatically in Fig. 1. *I.C.* is a large six-inch induction coil. Its primary is connected to a source of direct-current supply. *I* is a Cunningham mercury-jet interrupter. It has a wide range of frequency of interruption and when in good working order can be depended upon to give a constant root-mean-square current in the secondary of the induction coil. *C* is a condenser the plates of which are separated by sheets of glass which can resist differences of potential of 30,000 volts or more. This condenser, when charged by the induction coil to the point of breaking down the spark-gap *S*, discharges through the variable inductance *L*.

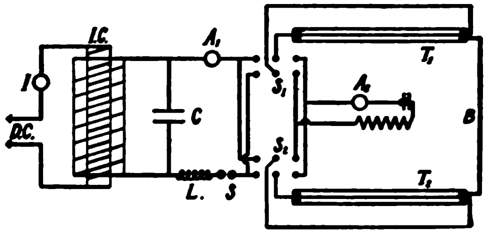

Fig. 1.

Possibly the greatest difficulty in maintaining the discharge of a condenser with sufficient constancy of current, to enable one to use it for precise measurements, lies in the spark-gap used. A long series of experiments showed conclusively that the electrodes must be clean and bright, and separated by an unvarying distance. Zinc electrodes, which are suitable for some purposes, are soon covered by an oxide which causes the width of the gap to vary. Fine jets of mercury were finally selected as the electrodes. The jets were perpendicular to each other in a horizontal plane and at the point of crossing were about a millimeter apart and half a millimeter in diameter. Their surfaces remained always clean and bright and the distances between them seemed to be unvarying. With these arrangements oscillating currents were obtained, adjustable in frequency from twenty thousand to ten millions or more cycles per second, and sufficiently uniform for precise measurements.

(*b*) *Measurement of Intensity of Current.*—In measuring the root-mean-square intensity of high frequency currents, it was found that several precautions were necessary. An instrument was first made which consisted of two parallel bars, each seven centimeters long, one centimeter wide and three millimeters thick. The bars were connected by seven No. 40 B. & S. gauge high resistance wires, placed one centimeter apart. A nickel-iron thermo-couple was soldered to the middle point of each wire and was properly calibrated by direct current. The alternating current leads were connected to the ends of the bars from the same side. It was found that with a direct current flowing through the instrument each resistance wire conducted one seventh of the total current. An alternating current of frequency about 300,000 was sent through the instrument and readings were taken from the thermo-couples. It was found that the ratio of currents in the two extreme wires was about seven to nine, with the wire nearest the leads carrying the most current. This unequal distribution shows the necessity for caution in the constuction of an ammeter that is to be used for alternating currents of high frequency.

To eliminate the danger of unequal current distribution an ammeter was made as is shown in Fig. 2. In place of the two parallel bars in the instrument described above, there were substituted two triangular blocks of copper, P_1 and P_2, with their parallel edges about three centimeters apart. The bases of the triangles measured 4 cm. and the altitudes 10 cm. The blocks were connected by fifteen no. 40 resistance wires, spaced about 2 mm. apart. On the center wire was soldered a thermo-couple *T.C.*, which is connected to a sensitive D'Arsonval galvanometer *G.* Resistance wires as small as no. 40 were used so that one could be sure that the alternating current resistance, for frequencies up to 1,000,000, was not noticeably different from the direct-current resistance, and hence the instrument could be calibrated by direct current. For currents ranging between one and two amperes, fifteen resistance wires gives about the best sensitiveness. This form of ammeter may be used for a very wide range of current strength by selecting a proper number of resistance wires.

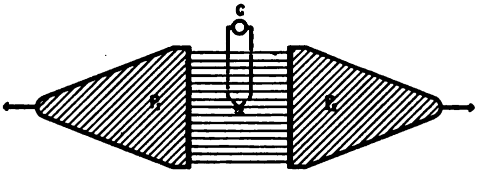

Fig. 2.

In using the latter instrument to obtain data for this paper each reading of alternating current was calibrated by direct current within a few minutes after the alternating currents had passed through it. This eliminates the danger of incorrect readings caused by a change in room temperature. A wooden box protected the instrument from any air-drafts.

(*c*) *Measurement of Frequency of Alternation.*—Fleming has devised an instrument for measuring the frequency of alternating currents which he calls a photographic spark counter.[1] Since it has been modified in some particulars it will be described here. There is first an enclosing box about 25 cm. square and 40 cm. high. See Fig. 3, which is a diagram showing the plan of the essential parts. A vertical shaft near the middle of one side has mounted on it a four-sided mirror, also a fly wheel to insure uniformity of rotation. A collimator tube projects from one side of the box in line with the mirror. The spark-gap is placed directly in front of the collimator tube. The light from the spark passes through a lens to the mirror and is there reflected at an angle of about ninety degrees to a slit in the side of the box. A suitable plateholder is held in front of the slit and is so constructed that the photographic plate may be raised or lowered by a string passing through the top of the holder. Ordinarily the plate was about twenty centimeters from the mirror. For the higher frequencies it was found necessary to extend the box so that the plate was about fifty centimeters from the mirror. The mirror was rotated by a motor driven by storage cells. The speed of rotation of the mirror could be made as much as one hundred revolutions per second, but was ordinarily rotated at a speed from sixty to eighty revolutions per second. A speed counter attached directly to the upper end of the mirror shaft, with the aid of a stop watch, gave a measure of the angular velocity of the mirror.

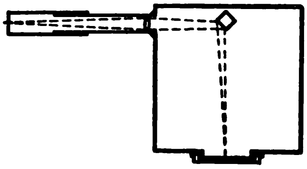

Fig. 3.

The plate was raised or lowered by hand since it was not necessary to know the velocity with which it moved. The projection of the train of oscillations on the plate could easily be made less than the width of the plate by properly modifying the speed of the motor. The sigma brand of Lumière plates was used with excellent results. The average distance between images of sparks was measured by means of calipers and standard scale. From the average distance between images, together with the dimensions of the apparatus involved, the frequency of the sparks was calculated. The accuracy of these measurements is probably within two or three per cent.

In early trials with the apparatus, it was found that the upper limit of frequency of sparks easily counted was about one million per second. At frequencies higher than this, the successive images of individual sparks were fused together into bands, thirty to fifty or sixty in number, each band representing a complete oscillatory discharge of the condenser, and the number of bands representing the number of discharges occurring in the well-known multiple manner. With lower frequencies the bands were drawn out into trains of oscillatory sparks. There were usually from twelve to eighteen complete oscillations in each train visible on the plate. Since the intensity of luminosity of the spark becomes gradually weaker, it is impossible to say how many oscillations there are in each train, for the sensitiveness of the plate limits the number of those that can be counted. The character of the photographs has been shown by a number of previous writers, among whom Trowbridge[1] has done extensive work.

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[1] *Loc. cit.*

(*d*) *The Differential Electric Thermometer.*—To compare the virtual resistance with the direct current resistance, a differential electric thermometer was used. This instrument was devised and used by Fleming.[2] As shown in Fig. 1 it consists of two glass tubes, T_1 and T_2, each about 125 cm. long and 4 cm. in diameter. They are as nearly alike as possible. A small tube with a bore about a millimeter in diameter connects the two larger tubes which are otherwise air-tight. The wires under test pass through rubber stoppers at the ends and complete the electric circuit through either S_1 or S_2, which are highly insulated, six-pole switches. These are used to connect the wire in either tube with the direct current or the oscillating current as may be desired. A small drop of ether or some other light liquid in the capillary tube will indicate any differences of heat generation in the tubes T. It is possible to balance the heat developed by an alternating current in one tube, by an equal amount of heat in the other tube. Since the heat produced in any circuit is proportional to the resistance and the square of the current, at the point of balance the ratio of resistances may be expressed as the inverse ratio of the squares of the currents. From the ammeters in the direct-current circuit and the alternating-current circuit the values of the two currents are read, and from these two readings the ratio of resistances is calculated. In order to minimize any error which might enter into the measurements, because of differences of specific heats of the glass in the two tubes, or in the amount of glass, or radiating power, the currents in the wires were interchanged a number of times and the average results taken.

It was necessary to arrange both the alternating-current circuits, one passing through T_1 and the other through T_2, so that in interchanging circuits during the course of a particular set of readings, there would be no difference of frequency. This was done by changing the area enclosed by one circuit until the frequency of the current in that circuit, as measured by means of the photographic plate, was the same as the frequency of the current when passing through the other circuit.

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[1] Trowbridge, Phil. Mag., August, 1894, p. 182.

[2] *Loc. cit.*

In taking any set of readings for a definite frequency, the method of procedure was to balance three or four different values of alternating current by direct current, with each value of alternating current passing through both circuits T_1 and T_2. The average of these six or eight readings was used to calculate the ratio of R' to R.

The oscillating spark was photographed by the spark counter during one of these readings. The average distance between images on the photographic plate was taken from three or four trains of images and this average distance used in calculating the frequency. The angular velocity of the mirror could be measured within two or three per cent. The frequency of the oscillations could probably be calculated within three or four per cent. of the correct value. The error in the measured ratio of R' to R is not more than four per cent. of the correct value.

(*e*) *Test of the Apparatus.*—In order to test the efficiency of the apparatus, cylindrical wires were introduced into the differential thermometer and observations made on the change of resistance. Another and more important reason for taking this preliminary set of readings, was to discover whether the damping of the oscillations was great enough to cause any appreciable difference between the observed ratio of resistance and that calculated by a formula based upon the assumption that the oscillations were undamped. The results are shown in Table I. Since the experimental readings are within less than one per cent. of the values calculated by Maxwell's formula, it may be assumed that the damping is small enough to neglect, and that the apparatus may be depended upon to give reliable readings, to the degree of precision indicated.

TABLE I.

Variation of Resistance of Cylindrical Wires. Copper Wire, No. 25 Brown and Sharpe Gauge, 0.045 cm. in Diameter.

Frequency.	R'/R Observed.	R'/R Calculated.
36,100	1.000	1.001
138,000	1.062	1.061
283,000	1.215	1.213
313,000	1.242	1.244

Maxwell's formula used in calculating R'/R in the above table is as follows:

$$\frac{R'}{R} = 1 + \frac{\pi^2 N^2 d^4}{48.\rho^2} - \frac{\pi^4 N^4 d^8}{2880.\rho^4} + \cdots,$$

where N is the frequency, d is the diameter of the wire and ρ is the specific resistance. For the wire used above $d = 0.045$ cm. and ρ was taken at 1,600.

To illustrate how the observed values of R'/R were obtained the following data are quoted for the case where the frequency was 283,000.

At the point of balance in the differential electric thermometer:

Avg. direct current through $T_1 = 1.725$ amps.
Avg. alt. " " $T_2 = 1.535$ "

$$R'/R = \left(\frac{\text{D.C.}}{\text{A.C.}}\right)^2 = 1.26,$$

Avg. direct " " $T_2 = 1.670$ "
Avg. alt. " " $T_1 = 1.546$ "

$$R'/R = \left(\frac{\text{D.C.}}{\text{A.C.}}\right)^2 = 1.17,$$

$$\text{Avg. } R'/R = 1.215.$$

The frequency was obtained from the following formula:

$$N = 4\pi\omega r/f = 283{,}000.$$

where ω, the speed of the mirror, = 70.4 revolutions per second,
r, the distance from the mirror to the plate, = 53.5 cm. and
f, the average distance between images on the plate, = 0.167 cm.

(*f*) *The Virtual Resistance of Wires of Square and Rectangular Cross-Section.*—In applying the formulas no. 31 and no. 27 (developed below) to the experimental results given in Fig. 4, it will be assumed that the effects of damping of the oscillating current are negligible. Formula (27) is more useful for calculating the ratio of apparent resistance to that offered to direct current, in the case of alternating currents of lower frequency.

The calculated values of the ratio of the virtual resistance to the direct-current resistance for the wire of which $2a = 0.059$ cm., were plotted as shown in Fig. 4. The curve is drawn from the calculated values and the small circles indicate the experimental observations.

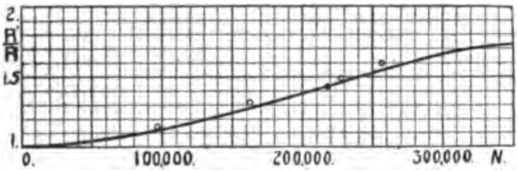

Fig. 4.

Fig. 5 shows in a similar manner the nearness with which the experi-

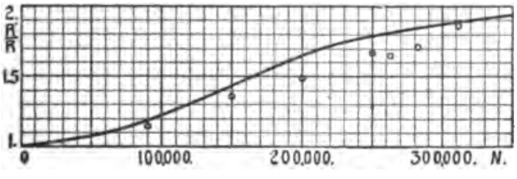

Fig. 5.

mental values check the calculated ones for the square-sectioned wire of which $2a = 0.070$ cm.

Replacing the square wires by wires of rectangular section, another series of observations was obtained, the results of which are shown in Fig. 6 and Fig. 7. The calculated values of R'/R for the wire of which $2a = 0.039$ cm. and $2b = 0.0665$ cm., were used in drawing the curve of Fig. 6, the small circles indicating, as above, the experimental readings.

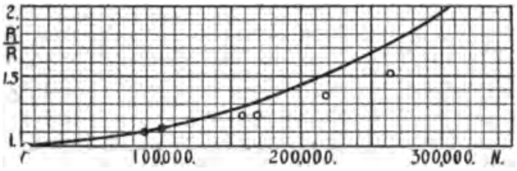

Fig. 6.

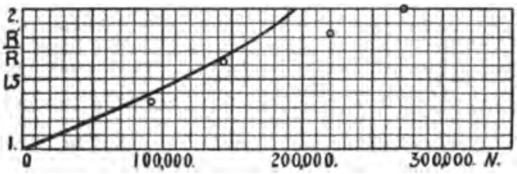

Fig. 7.

Similarly Fig. 7 was drawn for the wire of which $2a = 0.0485$ cm. and $2b = 0.127$ cm. With a wire as large as this last one, the formula does not give values which agree satisfactorily with the experimental values if the frequency is much greater than 150,000. Formulas (26) and (30) were used here in calculating the values for R'/R (see below).

3. Mathematical Development.

The conductor, rectangular in cross-section, is so long that end effects may be neglected. Other conductors are so far removed that their influence need not be considered. Referring to Fig. 8, a reference system is chosen, with the origin at the center of any cross-section, the X and Y axes parallel to the sides of the section, and the Z axis coinciding with the axis of the wire. Since the conductor is long, it may be assumed that no component of current flows parallel to the XY plane. The following equation then holds:

$$-4\pi\mu w = \frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2}, \tag{1}$$

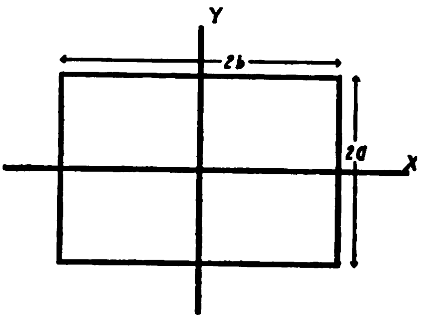

Fig. 8.

where, in agreement with Maxwell's notation, w is the z component of current intensity, H is the z component of vector potential of magnetic induction and μ is the permeability of the material of the conductor.

The impressed electromotive intensity may be supposed equal at all points of the cross-section of the wire, assuming that the specific resistance is uniform. Let the electromotive force per unit length be $E\epsilon^{int}$. Considering only instantaneous relations, the total electromotive intensity, inductive and non-inductive, in the wire is

$$P = E - \frac{\partial H}{\partial t}. \tag{2}$$

Outside the wire the corresponding electromotive intensity is

$$P = -\frac{\partial H}{\partial t}. \tag{3}$$

If the specific resistance of the wire is ρ and the specific inductive capacity of the medium is K

$$w = \left(\frac{1}{\rho} + \frac{inK}{4\pi}\right) P. \tag{4}$$

Considering the inductive action only,

$$P = -\frac{\partial H}{\partial t}, \tag{5}$$

and eliminating w between equations (1) and (4)

$$\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} - 4\pi\mu in\left(\frac{1}{\rho} + \frac{inK}{4\pi}\right) H = 0. \tag{6}$$

In the wire the current may be regarded as due to the conductivity alone, and if

$$k^2 = 4\pi\mu in/\rho$$

then

$$\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} - k^2 H = 0. \tag{7}$$

In the surrounding medium $1/\rho$ may be neglected and putting $h = n/V$, where V, the velocity of propagation of the disturbance, is $1/\sqrt{K\mu}$,

$$\frac{\partial^2 H}{\partial x^2}+\frac{\partial^2 H}{\partial y^2}+h^2H=0. \tag{8}$$

The general solution of (7) is

$$H=A\epsilon^{kx}+B\epsilon^{-kx}+C\epsilon^{ky}+D\epsilon^{-ky}+F\epsilon^{k'\overline{x+y}}+M\epsilon^{-k'\overline{x+y}}+N\epsilon^{k'\overline{x-y}}+Q\epsilon^{-k'\overline{x-y}}, \tag{9}$$

where $k'=k/\sqrt{2}$, and if $h'=h/\sqrt{2}$ the solution of (8) is

$$\begin{aligned}H=A'\epsilon^{ihx}+B'\epsilon^{-ihx}+C'\epsilon^{ihy}+D'\epsilon^{-ihy}+F'\epsilon^{ih'\overline{x+y}}+M'\epsilon^{-ih'\overline{x+y}}&\\ +N'\epsilon^{ih'\overline{x-y}}+Q'\epsilon^{-ih'\overline{x-y}}.&\end{aligned} \tag{10}$$

By symmetry relations the value of H must remain unchanged if $+x$ is written for $-x$ and $+y$ for $-y$ in the equations (9) and (10). This shows at once that $A=B$, $A'=B'$, $C=D$, $C'=D'$, $F=M=N=Q$ and $F'=M'=N'=Q'$. Hence inside the wire

$$H=2A\cosh kx+2C\cosh ky+2F\,(\cosh k'\overline{x+y}+\cosh k'\overline{x-y}), \tag{11}$$

and outside

$$H=2A'\cosh ihx+2C'\cosh ihy+2F'\,(\cosh ih'\overline{x+y}+\cosh ih'\overline{x-y}). \tag{12}$$

If the wire has a square cross-section instead of a rectangular section then x can be interchanged with y in (11) and (12) without affecting H. This necessitates the additional simplification that $A=C$ and $A'=C'$.

To evaluate the constants of (11) and (12), the continuity of the total electromotive intensity and magnetic field intensity, at the boundary, is used. If α and β are the x and y components of magnetic field intensity, then since the curl of the vector potential is the magnetic field intensity, at the point $x=b$, $y=0$, by the continuity of β the following relation is obtained from (11) and (12):

$$kA\sinh kb+2k'F\sinh k'b=ihA'\sinh ihb+2ih'F'\sinh ih'b. \tag{13}$$

Similarly by the continuity of α at $x=0$, $y=a$,

$$kC\sinh ka+2k'F\sinh k'a=ihC'\sinh iha+2ih'F'\sinh ih'a. \tag{14}$$

Also at the point $x=b$, $y=a$, for both α and β,

$$\begin{aligned}kA\sinh kb+k'F\,(\sinh k'\overline{b+a}+\sinh k'\overline{b-a})&=ihA'\sinh ihb\\ &\quad+ih'F'(\sinh ih'\overline{b+a}+\sinh ih'\overline{b-a}),\end{aligned} \tag{15}$$

$$\begin{aligned}kC\sinh ka+k'F\,(\sinh k'\overline{b+a}-\sinh k'\overline{b-a})&=ihC'\sinh ih'a\\ &\quad+ih'F'(\sinh ih'\overline{b+a}-\sinh ih'\overline{b-a}).\end{aligned} \tag{16}$$

Also by the continuity of the total electromotive intensity at $x = b$ $y = 0$ and at $x = 0$, $y = a$ using equations (2) and (3), two more relations may be obtained:

$$E - 2inA \cosh kb - 4inF \cosh k'b = -2inA' \cosh ihb - 2inF' \cosh ih'b, \quad (17)$$

$$E - 2inC \cosh ka - 4inF \cosh k'a = -2inC' \cosh iha - 2inF' \cosh ih'a. \quad (18)$$

From equations (13) to (18) the values of the constants may be found.

The total current passing through any cross-section may be found by taking the line integral of the magnetic field intensity around the boundary. If γ is the total current

$$\gamma = 4\int_0^a \beta dy - 4\int_0^b \alpha dx. \quad (19)$$

Inserting the values of α and β in this equation and integrating gives the desired electromotive force equation, from which, expressions for the virtual resistance and inductance may be calculated. The determinations of the constants by equations (13) to (18) is so complicated as to be unmanageable. It is possible, however, to obtain approximate formulas with mean value for the constants by assuming that $A = C = F$ in equation (11) and neglecting the effect of the medium. The assumption that $A = C$ means that the vector potential along the x axis is the same as along the y axis for equal values of the argument. This is true for a square sectioned wire but when considering a rectangular sectioned conductor it is only approximately true, the degree of approximation depending upon the difference between the two dimensions. The justification for putting $A = F$ is based upon the substantiation of the results as calculated for particular cases from experimental observations. The values of R'/R for four particular cases, calculated by a formula based upon this assumption are given in Figs. 5–8. Since the observed values agree up to frequencies of 150,000, with these calculated values, it must be that up to this limit F is nearly equal to A. For the two rectangular sectioned wires this limit is reached at frequencies of 150,000 and then the formulas fail, then the differences between the observed and calculated values increases as the frequency increases. For the larger square sectioned wire the values agree within five per cent. up to a frequency of 150,000, and then the differences increase to about ten per cent. at a frequency of 265,000, and at 312,000 the values are again in close agreement. The differences for the smaller square sectioned wire are not greater than three per cent. for the range tested, namely up to a frequency of 257,000.

To obtain these approximate expressions equation (7) will be used, but put into more convenient form. Introducing the non-inductive part of the electromotive intensity, which may be called $\partial\psi/\partial z$, into equation (4) and neglecting the effect of the medium, gives

$$\rho w = -\frac{\partial\psi}{\partial z} - \frac{\partial H}{\partial t}. \tag{20}$$

Eliminating w between this equation and equation (1)

$$\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} - k^2\left(H - \frac{i}{n}\frac{\partial\psi}{\partial z}\right) = 0. \tag{21}$$

Since $\frac{i}{n}\frac{\partial\psi}{\partial z}$ is independent of x or y, (21) may be written

$$\frac{\partial^2\left(H - \frac{i}{n}\frac{\partial\psi}{\partial z}\right)}{\partial x^2} + \frac{\partial^2\left(H - \frac{i}{n}\frac{\partial\psi}{\partial z}\right)}{\partial y^2} - k^2\left(H - \frac{i}{n}\frac{\partial\psi}{\partial z}\right) = 0. \tag{22}$$

The general solution of this equation is similar to the solution of (7) and has eight undetermined coefficients. This number may be reduced to three by the symmetry relations as is shown above. Assuming now that these three constants are all equal leads to the following solution:

$$H = \frac{i}{n}\frac{\partial\psi}{\partial z} + 2A(\cosh kx + \cosh ky + \cosh k'\overline{x+y} + \cosh k'\overline{x-y}). \tag{23}$$

The value of the single undetermined coefficient may be found by integrating the expression for current intensity over the surface of the cross-section. If γ is the total current,

$$\gamma = 4\int_0^a\int_0^b w\,dy\,dx.$$

Using the value of w as determined by equations (1) and (23), with the aid of the above integral, the value of A may be shown to be

$$A = -\frac{\pi\mu\gamma}{2(ka\sinh kb + kb\sinh ka + 2\cosh k'\overline{b+a} - 2\cosh k'\overline{b-a})}. \tag{24}$$

If at the point $x = b$, $y = 0$, H is put equal to some constant, say L, times the current and if l be the length of the conductor considered, multiplying equation (23) by lin and putting $-l\frac{\partial\psi}{\partial z} = E$, the electromotive force, gives

$$E = Llin\gamma$$

$$+ lin\pi\mu\gamma\frac{\cosh kb + 2\cosh k'b + 1}{ka\sinh kb + kb\sinh ka + 2\cosh k'\overline{b+a} - 2\cosh k'\overline{b-a}}. \tag{25}$$

If the hyperbolic functions are expanded in series of powers of k and the numerator divided by the denominator, the following expression is obtained:

$$
\begin{aligned}
E = lin\gamma & \left[L + \frac{\pi\mu(2b^2 - a^2)}{12ab} - \frac{\pi^5\mu^3N^2(-b^6 + 140b^4a^2 + 56b^2a^4 - 29a^6)}{3780 \cdot ab\rho^2} + \cdots \right] \\
& + R\gamma \left[1 + \frac{\pi^4\mu^2N^2(4b^4 + 30b^2a^2 - 11a^4)}{45\rho^2} \right. \qquad (26) \\
& \left. - \frac{\pi^8\mu^4N^4(-172b^8 + 1070b^6a^2 + 2807b^4a^4 - 340b^2a^6 - 142a^8)}{14175 \cdot \rho^4} + \cdots \right].
\end{aligned}
$$

where $R = l\rho/4ab$ (the resistance of a length l for direct current) and $N = n/2\pi$, the number of alternations per second. Writing R' for the virtual resistance, gives

$$\frac{R'}{R} = 1 + \frac{\pi^4\mu^2N^2(4b^4 + 30b^2a^2 - 11a^4)}{45\rho^2} - \cdots. \qquad (27)$$

If the wire has a square cross-section the expression for the virtual resistance may be found by putting $b = a$ in (26)

$$\frac{R'}{R} = 1 + \frac{23\pi^4\mu^2N^2a^4}{45\rho^2} - \frac{3223\pi^8\mu^4N^4a^8}{14175 \cdot \rho^4} + \cdots. \qquad (27)$$

Formulas (26) and (27) may be used in calculating R'/R for particular cases where the dimensions and frequency are of a magnitude which will give a value of 0.5 or less to the second term of the series. If the frequency and dimensions are large then the series is not rapidly convergent. The calculation of more terms of the series is troublesome. To obtain a complete expression the fraction in (25) may be expressed in exponential functions and then separated into real and imaginary parts. The real coefficient of γ is then the desired expression for R'. The device used in making the necessary transformation is embodied in the following relations:

$$k = \sqrt{2i}\sqrt{\frac{2\pi\mu n}{\rho}} = (1 + i)S,$$

where

$$S = \sqrt{\frac{2\pi\mu n}{\rho}}. \qquad (28)$$

Hence each hyperbolic function may be expressed in somewhat the following manner:

$$\cosh kb = \tfrac{1}{2}(e^{kb} + e^{-kb}) = \cos bS \cosh bS + i \sin bS \sinh bS.$$

Making these substitutions in (25) and then rationalizing the denominator of the fraction, gives

$$E = Llin\gamma + lin\pi\mu\gamma \frac{(A_1C_1 + B_1D_1) + i(B_1C_1 - A_1D_1)}{C_1^2 + D_1^2}, \tag{29}$$

where

$$A_1 = \cos bS \cosh bS + 2 \cos \frac{bS}{\sqrt{2}} \cosh \frac{bS}{\sqrt{2}} + 1,$$

$$B_1 = \sin bS \sinh bS + 2 \sin \frac{bS}{\sqrt{2}} \sinh \frac{bS}{\sqrt{2}},$$

$$C_1 = aS \cos bS \sinh bS - aS \sin bS \cosh bS + bS \cos aS \sinh aS$$
$$- bS \sin aS \cosh aS + 2 \cos \frac{b+a}{\sqrt{2}} S \cosh \frac{b+a}{\sqrt{2}} S - 2 \cos \frac{b-a}{\sqrt{2}} S \sinh \frac{b-a}{\sqrt{2}} S,$$

$$D_1 = aS \cos bS \sinh bS + aS \sin bS \cosh bS + bS \cos aS \sinh aS$$
$$+ bS \sin aS \cosh aS + 2 \sin \frac{b+a}{\sqrt{2}} S \sinh \frac{b+a}{\sqrt{2}} S - 2 \sin \frac{b-a}{\sqrt{2}} S \sinh \frac{b-a}{\sqrt{2}} S.$$

Hence:

$$\frac{R'}{R} = \frac{4n\pi\mu ab}{\rho} \times \frac{A_1D_1 - B_1C_1}{C_1^2 + D_1^2}. \tag{30}$$

For the wire of square cross-section this expression becomes simplified and

$$\frac{R'}{R} = \frac{4\pi n\mu a^2}{\rho} \times \frac{A_2D_2 - B_2C_2}{C_2^2 + D_2^2}, \tag{31}$$

where the change in subscripts indicate the changes in the constants which are obtained by putting $b=a$.

It is shown above that these expressions can be used to calculate the virtual resistance within certain limits.

Before leaving the mathematical side of the investigation an expression for finding the intensity of current at any point of the cross-section of the conductor is to be developed. For present purposes a study of the distribution of current in a wire of square cross-section is just as instructive as that in a wire of rectangular cross-section.

Using equation (1) for current intensity and (23) for vector potential the following expression, for the wire of square section, is obtained:

$$4w = \frac{\gamma[k^2(\epsilon^{kx} + \epsilon^{-kx} + \epsilon^{ky} + \epsilon^{-ky}) + k'^2(\epsilon^{k'\overline{x+y}} + \epsilon^{-k'\overline{x+y}} + \epsilon^{k'\overline{x-y}} + \epsilon^{-k'\overline{x-y}})]}{2(\epsilon^{2k'a} + \epsilon^{-2k'a}) + 2ka(\epsilon^{ka} - \epsilon^{-ka}) - 4}. \tag{32}$$

The exponential functions of this expression may be separated into real and imaginay parts by a method of procedure similar to the method used above.

$$4w = \frac{\gamma S^2[(A_3C_3 - D_3B_3) + i(A_3D_3 + B_3C_3)]}{C_3^2 + D_3^2}, \tag{33}$$

where

$$A_3 = -\left[\sin Sx \sinh Sx + \sin Sy \sinh Sy + \sin\frac{x+y}{\sqrt{2}}S \sinh\frac{x+y}{\sqrt{2}}S \right.$$
$$\left. + \sin\frac{x-y}{\sqrt{2}}S \sinh\frac{x-y}{\sqrt{2}}S\right],$$

$$B_3 = \cos Sx \cosh Sx + \cos Sy \cosh Sy + \cos\frac{x+y}{\sqrt{2}}S \cosh\frac{x+y}{\sqrt{2}}S$$
$$+ \cos\frac{x-y}{\sqrt{2}}S \cosh\frac{x-y}{\sqrt{2}}S,$$

$$C_3 = \cos\sqrt{2}\,aS \cosh\sqrt{2}\,aS + aS \cosh aS \sinh aS - aS \sin aS \cosh aS - 2,$$
$$D_3 = \sin\sqrt{2}\,aS \sinh\sqrt{2}\,aS + aS \cos aS \sinh aS + aS \sin aS \cosh aS.$$

The equation (33) expressing current intensity at any point in the cross-section of the wire is like the general electromotive force equation in that it is a complex quantity. The form must be complex because part of the current is caused by the inductive action and the other part by the non-inductive action. If equation (33) were multiplied by ρ, the specific resistance, the resulting equation would be an electromotive force equation, which is in general complex.

To obtain values of w at points in the cross-section of a particular wire under given conditions, the real and imaginary parts must be calculated separately, and then added by vector methods, or analytically by finding the square root of the sum of their squares.

4. VARIATION OF CURRENT INTENSITY.

Another purpose of this paper is to show the variation of current intensity or density of flow, over the sectional area of a long, straight conductor of square cross-section, carrying current of high frequency. The mathematical development leads to a computation of current intensity at any point of the section. Since no experimental method of measuring this quantity has thus far been devised, the equations derived from theoretical considerations will be relied upon entirely. The justification for this course lies in the satisfactory agreement between experimental and theoretical results, already described in another part of this paper. It appears that the experimental difficulties in the measurement of current intensity would be considerable. If the wire be separated into filaments, like the fine, parallel wires of a flexible cable, the conditions which cause the uneven distribution of current have been modified to such an extent that the measurement of current in each filament would be of little value in solving the problems proposed. Equation (33) will be used in the calculations which follow.

A wire or bar, two centimeters square, has been selected for illustration. To simplify the calculation let the frequency be $400/\pi^2$. This makes S of equation (33) unity. Since the wire is large in cross-section, even with low frequency the variation in current intensity will be similar to the variation in a smaller wire with higher frequency. The similarity may be seen from an inspection of formula (32). It will be noticed that wherever $\sqrt{N}$ appears in the equation as a factor, a dimensional length x, y or a appears also as a factor. N appears elsewhere only in K^2. If $\sqrt{N}d$ (where d is a dimension) is put equal to some constant, then $\sqrt{N}$ and d may be varied individually, so long as their product remains constant, and the resulting value for w will be proportional to the frequency.

Consider the square section as a special case of the rectangular section of Fig. 8 in which b equals a. Fig. 9 shows graphically the variation of current intensity along the three principal lines of the particular square selected. Curve A represents the variation from the origin along the line $y = 0$ to $x = \pm a$. Curve B shows the variation from the middle of any side on either axis along the edge to the vertex. This curve represents the symmetrical variation of current along eight different lines of the square. In curve C the variation of current intensity along a diagonal from the origin to any one of the four vertices is shown.

Another graphical representation of the density of current flow over the section of the same square wire, at the same frequency of alternation, is made in Fig. 10. Here contour lines are drawn for one quadrant of the section, the difference between consecutive lines being 0.005 C.G.S. unit of current. The line nearest the origin indicates an intensity of 0.215 C.G.S. unit. The current is fairly uniform over the central region, but proceeding from the origin along a diagonal to a vertex the lines are drawn more closely together. It might be supposed at first sight that for the case of very high frequency the current would be localized entirely at the corners. That such is not the case may be seen by inspection of formula (33). Putting x and y both equal to zero, the numerator still contains N, which, although small in comparison with the denominator, gives w a value different from zero.

In any electromagnetic phenomenon the law of the conservation of energy is valid. In circuits such as described above the energy is manifested in two ways, namely, in the production of heat and in the production of the magnetic field. There would be a minimum of heat produced if the current were distributed uniformly over the cross-section. The energy of the magnetic field would be a minimum if the current were entirely on the surface of the wire. Since both of these conditions cannot be satisfied simultaneously, a compromise is established which makes the total energy a minimum. This compromise is shown for a particular case in Fig. 11.

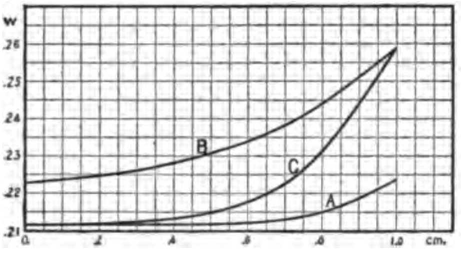

Fig. 9.

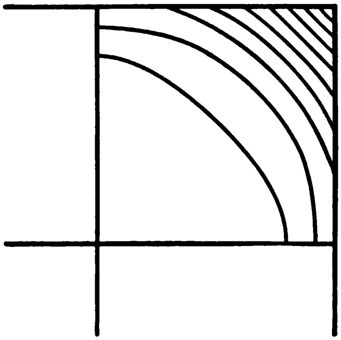

Fig. 10.

To show the variation in current intensity for different frequencies, also to show that the variation in a small wire with high frequency is similar to the variation in a large wire with low frequency, the values of *w* for a wire having $2a = 0.070$ cm., with a frequency of 101,320, have been calculated along the line corresponding to curve *A* of Fig. 9 and are shown in Fig. 11. The increase in intensity from the smallest to the greatest value in the smaller wire is greater than in the larger wire, but the characteristics of the two curves are the same. A value of the frequency could be found that would make the increase the same in both wires.

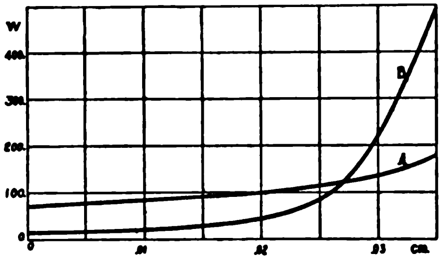

Fig. 11.

The effect of increasing the frequency of alternation of current in the same wire of square section is illustrated by the two curves of Fig. 11. Both curves are for the line $y = 0$ from the origin to $x = a$. The length of one side of the section is $2a = 0.070$ cm. Curve *A* shows the variation for a frequency of 101,320, and curve *B* for a frequency of

1,000,000. The wire is supposed to carry the same total current in both cases, ten amperes. The effect of increasing the frequency is shown in a crowding of the current toward the boundaries of the wire.

SUMMARY.

1. Alternating currents have been produced by the discharge of a condenser through an inductive resistance, with sufficient uniformity of current to render possible their use in precise measurements.

2. An ammeter is described which is suitable for the measurement of the intensity of alternating currents.

3. The frequency of alternating currents has been measured by a photographic spark counter for any frequency up to three quarters of a million per second.

4. By checking Maxwell's formula for the virtual resistance of cylindrical wires, it is shown that the damping of the oscillating currents used is small enough to neglect.

5. The ratio of the virtual to the direct current resistance for copper wires of square and rectangular cross-section was measured by the use of a differential thermometer, and these observed values were checked by approximate formulas within certain limits. For the two square cross-sectioned wires tested this limit was for frequencies above one hundred and fifty thousand and for the two rectangular cross-sectioned wires the limit was about one hundred and fifty thousand.

6. Formulas are developed by certain assumptions in the general theory, which give approximate methods of calculating the ratio of the virtual to the direct current resistance. The validity of these assumptions is based upon experimental results.

7. In the development of the expression from which the ratio of resistances is calculated, there occurs an expression for current intensity at any point of the cross-section of the conductor. This expression is used to calculate, for some particular cases, the distribution of current intensity within the cross-section.

UNIVERSITY OF CALIFORNIA,
May 1, 1911.

ON THE NOMENCLATURE OF CRYSTALLOGRAPHY.

By Paul Saurel.

THE thirty-two types of crystal symmetry have received so many different names that it may seem useless to add to the reigning confusion by offering a new set. And yet the nomenclature and the symbols which I wish to suggest recall so simply the characteristic elements of symmetry of each of the thirty-two types that I cannot refrain from submitting them to the judgment of physicists.

But first it will be necessary to recall briefly the various possible types of symmetry. It is well known that the only elements of symmetry that need be considered are a center of symmetry, axes of direct symmetry and axes of inverse symmetry.[1] The point O is said to be a center of a symmetry of a system if to every point P of the system there corresponds a point P' of the system such that the line PP' is bisected by the point O. The points P and P' are said to be inverses of each other with respect to the center O, and instead of saying that the system possesses a center of symmetry we may say that inversion with respect to O transforms the system into itself. A line OA is said to be an axis of direct symmetry of order n if rotation of the system about OA through an angle equal to $1/n$th of an entire revolution causes every point of the system to take a position previously occupied by a point of the system. Thus we may say that rotation about an axis of direct symmetry transforms the system into itself. Finally, a line OA is said to be an axis of inverse symmetry of order n if rotation about OA through an angle equal to $1/n$th of an entire revolution followed by an inversion with respect to O transforms the system into itself.

The various possible types of symmetry fall into four groups: (1) the types that are characterized by the existence of axes of direct symmetry alone; (2) the types that are characterized by the presence of a center of symmetry; (3) the types that are characterized by the presence of axes of inverse symmetry without a center of symmetry; (4) the type that is characterized by the absence of all elements of symmetry.

The types of symmetry that are characterized by the existence of axes of direct symmetry alone are five in number which, following the usage of mathematicians, we shall call the cyclic type, the dihedral type, the tetrahedral type, the octahedral type and the icosahedral type.

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[1] For demonstrations of the various statements made in the text the reader is referred to H. A. Lorentz, "Über die Symmetrie der Kristalle"; Abhandlungen über Theoretische Physik, Vol. 1, 1907, p. 299, and to Paul Saurel, "On the Classification of Crystals," Bulletin of the American Mathematical Society, Vol. 17, 1911, p. 398.

The cyclic type of symmetry is characterized by the presence of a single axis of direct symmetry of order n, where n is any integer except 1. We shall use the symbol C_n to represent this type of symmetry. Moreover, we shall agree to use the symbol C_1 to denote the absence of all symmetry.

The dihedral type of symmetry is characterized by the axes of symmetry which a regular polygon of n sides possesses. These consist of an n-ary axis perpendicular to the plane of the polygon and passing through its center, a set of n binary axes consisting of the radii drawn from the center of the polygon to its vertices, and a second set of n binary axes consisting of the radii drawn from the center of the polygon to the mid-points of its sides. The above general statement is to be understood to include the case $n = 2$; for this purpose it is necessary to agree to use the expression regular polygon of two sides to denote a limited straight line lying in a given plane. The axes of symmetry in this case consist of a binary axis perpendicular to the given plane and passing through the mid-point of the line, a pair of binary axes drawn from the mid-point of the line to its ends and a pair of binary axes lying in the given plane and drawn perpendicular to the given line from its mid-point. We shall use the symbol $D_{2,2,n}$ to denote the dihedral type of symmetry; the subscripts recall the orders of the axes.

The tetrahedral type of symmetry is characterized by the axes of symmetry which a regular tetrahedron possesses, namely, four ternary axes connecting the vertices of the tetrahedron with the mid-points of the opposite faces and three binary axes connecting the mid-points of opposite edges. We shall use the symbol $T_{2,3,3}$ to represent this type of symmetry.

The octahedral type of symmetry is characterized by the axes of symmetry which a regular octahedron possesses, namely, three quaternary axes connecting opposite vertices, four ternary axes connecting the mid-points of opposite faces, and six binary axes connecting the mid-points of opposite edges. We may also say that this type of symmetry is characterized by the axes of symmetry which a cube possesses, namely, three quaternary axes connecting the mid-points of opposite faces, four ternary axes connecting opposite vertices, and six binary axes connecting the mid-points of opposite edges. We shall use the symbol $O_{2,3,4}$ to represent this type of symmetry; the subscripts recall the orders of the axes.

The icosahedral type of symmetry is characterized by the axes of symmetry which a regular icosahedron possesses, namely, six quinary axes connecting opposite vertices, ten ternary axes connecting the mid-points of opposite faces, and fifteen binary axes connecting the mid-points of opposite edges. We may also say that this type of symmetry is characterized by the axes of symmetry which a regular dodecahedron possesses, namely, six quinary axes connecting the mid-points of opposite faces, ten ternary axes connecting opposite vertices, and fifteen binary axes connecting the mid-points of opposite edges. We shall use the symbol $I_{2,3,5}$ to represent this type of symmetry; the subscripts recall the orders of the axes.

From the types of symmetry C_n, $D_{2,2,n}$, $T_{2,3,3}$, $O_{2,3,4}$, $I_{2,3,5}$, characterized by the presence of axes of direct symmetry alone, it is easy to obtain the types of symmetry that are characterized by the presence of a center of symmetry. It is sufficient, indeed, to add to the axes of symmetry of each type a center of symmetry. We thus obtain five new types of symmetry which we shall denote by the symbols $\bar{C}_n$, $\bar{D}_{2,2,n}$, $\bar{T}_{2,3,3}$, $\bar{O}_{2,3,4}$, $\bar{I}_{2,3,5}$, and which we shall call the centro-cyclic, the centro-dihedral, the centro-tetrahedral, the centro-octahedral and the centro-icosahedral types; the bar will serve to recall the existence of a center of symmetry.

Finally from the types of symmetry characterized by direct axes of symmetry it is easy to obtain the types of symmetry characterized by the presence of inverse axes of symmetry. In the first place, from the cyclic type of even order C_{2n}, we obtain a new type of symmetry by replacing the direct axis of order $2n$ by an inverse axis of the same order. We shall denote this type by the symbol $C_{\overline{2n}}$, and we shall call it the inverse cyclic type. In the second place, from the dihedral type $D_{2,2,n}$, and the octahedral type $O_{2,3,4}$ we obtain new types of symmetry by replacing any two sets of direct axes of even order by inverse axes of the same orders. We shall denote these new types by the symbols $D_{\bar{2},\bar{2},n}$, $D_{2,\bar{2},\overline{2n}}$ where $n > 1$, $O_{\bar{2},3,\bar{4}}$ and we shall call them the inverse dihedral types of the first and second kind, and the inverse octahedral type. The bars, of course, serve to recall the axes of inverse symmetry.

The various types of symmetry are summarized in the following table.

Types of Symmetry characterized by

Axes of Direct Symmetry	Center of Symmetry	Axes of Inverse Symmetry	
C_n	$\bar{C}_n$	$C_{\overline{2n}}$	$n \geqq 1$
$D_{2,2,n}$	$\bar{D}_{2,2,n}$	$D_{\bar{2},\bar{2},n}$, $D_{2,\bar{2},\overline{2n}}$	$n \geqq 2$
$T_{2,3,3}$	$\bar{T}_{2,3,3}$		
$O_{2,3,4}$	$\bar{O}_{2,3,4}$	$O_{\bar{2},3,\bar{4}}$	
$I_{2,3,5}$	$\bar{I}_{2,3,5}$		

Not all of the types of symmetry enumerated in this table are available as types of crystal symmetry, for the law of rational indices limits the acceptable axes of symmetry to those of orders 1, 2, 3, 4, 6. With this limitation the table furnishes the 32 types of crystal symmetry, 11 from each of the first two columns and 10 from the third. These 32 types of symmetry fall naturally into six groups; the first group consists of the types that correspond to the regular solids, the second group consists of the types that contain a senary axis, while the third, fourth, fifth and sixth groups consist respectively of the types that contain a quaternary, a ternary, a binary or no axis. The following table contains the symbols and the names which are proposed for each of the thirty-two types of crystal symmetry; the names and especially the symbols recall concisely the characteristic elements of symmetry of the various types.

Regular System.

1. $\bar{O}_{2,3,4}$ Centro-octahedral type.
2. $O_{2,3,4}$ Octahedral type.
3. $O^{-}{}_{,\bar{3},4}$ Inverse octahedral type.
4. $\bar{T}_{2,3,3}$ Centro-tetrahedral type.
5. $T_{2,3,3}$ Tetrahedral type.

Senary System.

1. $\bar{D}_{2,2,6}$ Centro-dihedral type.
2. $D_{2,2,6}$ Dihedral type.
3. $D_{\bar{2},\bar{2},6}$ First inverse dihedral type.
4. $D_{2,\bar{2},\bar{6}}$ Second inverse dihedral type.
5. $\bar{C}_{6}$ Centro-cyclic type.
6. C_{6} Cyclic type.
7. C^{-} Inverse cyclic type.

Quaternary System.

1. $\bar{D}_{2,2,4}$ Centro-dihedral type.
2. $D_{2,2,4}$ Dihedral type.
3. $D_{\bar{2},\bar{2},4}$ First inverse dihedral type.
4. $D_{2,\bar{2},\bar{4}}$ Second inverse dihedral type.
5. $\bar{C}_{4}$ Centro-cyclic type.
6. C_{4} Cyclic type.
7. $C_{\bar{4}}$ Inverse cyclic type.

Ternary System.

1.	$\bar{D}_{2,2,3}$	Centro-dihedral type.
2.	$D_{2,2,3}$	Dihedral type.
3.	$D_{\bar{2},\bar{2},3}$	Inverse dihedral type.
4.	$\bar{C}_3$	Centro-cyclic type.
5.	C_3	Cyclic type.

Binary System.

1.	$\bar{D}_{2,2,2}$	Centro-dihedral type.
2.	$D_{2,2,2}$	Dihedral type.
3.	$D_{\bar{2},\bar{2},2}$	Inverse dihedral type.
4.	$\bar{C}_2$	Centro-cyclic type.
5.	C_2	Cyclic type.
6.	C^{-}	Inverse cyclic type.

Anaxial System.

1.	$\bar{C}_1$	Centric type.
2.	C_1	Acentric type.

New York, April 25, 1911.

ON THE POSITIVE POTENTIAL OF METALS IN THE PHOTOELECTRIC EFFECT AND THE DETERMINATION OF THE WAVE-LENGTH EQUIVALENT OF ROENTGEN RAYS.

By Jakob Kunz.

IT has been stated in two previous papers, published in this journal,[1] that the positive potential acquired by alkali metals under the action of visible light, presents different features in the red end and the blue end of the spectrum. In the red end the positive potential acquires a maximum as function of the frequency and depends on the intensity of the light; towards the violet end, however, the positive potential is largely independent of the intensity of the incident light, and increases proportional to the square of the frequency. When the intensity of the light used becomes very small, then the positive potential apparently depends on the intensity, but this is very likely due to the fact that the insulation is not perfect, so that the positive potential measured by the electrometer, never rises to that constant value which it acquires if the number of electrons emitted by the metal is larger. Nevertheless it is necessary to find out by means of experiments whether the positive potential in the ultra-violet region increases continuously with the square of the frequency or whether there is a second maximum similar to that in the red end of the spectrum. If this be the case, then we are dealing with phenomena of optical resonance alone while in the other case, where the positive potential increases with the square of the frequency, the phenomenon would be of a different character and would give an exact means of measuring the thickness of the pulse or the wave length equivalent of Roentgen rays, γ-rays and secondary Roentgen radiation.

Two different methods of measuring the positive potentials have been used. The first method was described in the previous papers, the positive potential being measured by means of an electrometer of high sensitiveness. That part of the tube which contained the alkali metal consisted of a quartz tube, or of a glass tube of the shape of Fig. 1, covered with a plate of quartz *C*. The quartz plate was sealed to the ground glass tube by means of Kotinsky cement, so that a very good vacuum could be obtained and increased by means of charcoal and liquid air. The alkali metal was introduced into *D* by means of a system of tubes and funnels as described before. It was found to be very important to use a perfectly clean metallic surface as a trace of impurity on the surface decreased the positive potential considerably or even annulled it. Thus the funnels had an opening of about 0.6 mm. diameter. An electrode made connection between the positive metal and the electrometer. Two negative electrodes *A* and *B* were used. *A*, a fine wire net blackened with lamp black, was introduced in order to establish an auxiliary potential difference between *A* and the aluminum electrode *B*, through which reflection of electrons from *B* might be prevented. The incidence of the ultra-violet light was perpendicular so as to prevent the reflected light from falling on the negative electrode *B*, and producing a positive potential.

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[1] Phys. Rev., Vol. XXIX., No. 3, September, 1909, p. 227; Vol. XXXI., No. 5, November, 1910, p. 538.

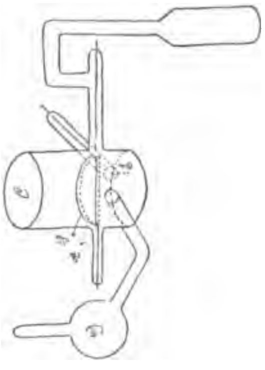

Fig. 1.

The ultra-violet light was produced by the discharge from a 3-kilowatt transformer between cadmium zinc and copper terminals in parallel with a suitable capacity, of three or four Leyden jars. The light passed through a specially prepared spectroscope, quartz lenses and a Cornu prism. The light incident upon the metal was always focused on the surface by a displacement of the last lens in the spectroscope.

The metals cæsium and rubidium were prepared by the following method: 14 gr. cæsium chloride molten in a stream of dry hydrochloric acid gas are mixed after cooling with 2.5 gr. commerical calcium, placed in an iron boat and in a tube of Bohemian glass; a plug of clean asbestos and iron wire keep the boat in a given position and prevent the mixture from spreading together with the metal vapor to the lower part of the glass tube, which is connected by means of glass tubes and sealing wax with the system of tubes, of Fig. 1. The glass tube is gradually heated to bright red heat, where the cæsium distils off and flows down into the receptacle. The distillation carried out in the vacuum yields very good results. The reduction of the cæsium chloride by calcium is almost complete. It takes place with a certain violence, even when the cæsium or rubidium chloride and the calcium have been dried as carefully as possible. It is therefore necessary to apply the plug of asbestos behind the iron boat in order to keep back the mixture.

The frequencies of the line spectra of zinc and cadmium were determined in the following way: The line spectrum was photographed and the photograph compared with the line spectrum on a transparent willemite screen. The characteristic lines on the willemite screen could be identified with the lines on the photographic plate without difficulty. Only those lines, which appeared on the willemite screen were allowed to act on the metal.

The strongest lines on the photographic plates are indicated by the following table.

Cd.	Zn.	Cu.
3615	3345	2769
2748	3302	2766
2573	2771	2369
2329	2756	2303
2321	2558	2294
2313	2502	2276
2288	2138	2242
2265	2064	2199
2144	2025	2149

Only those lines which produce phosphorescence on the willemite screen were allowed to affect the metal. The results of these measurements are given in the following tables, where l = wave-length, d = deflection, n = frequency, v = volts.

Cd Light.

l	$n \times 10^{-14}$	$n^2 \times 10^{-28}$	Na—K		Cæsium.	
			d	v	d	v
533.8	5.62	31.58	10.0	0.31	26.0	0.945
441.6	6.793	46.15	15.23	0.473	39.0	1.38
274.8	10.917	119.22	62.80	1.942	98.2	3.57
257.3	11.660	135.9	73.94	2.290	111.7	4.06
232.9	12.881	165.9	93.10	2.883	136.4	4.96
214.4	13.993	195.8	114.2	3.540	161.3	5.85

Zinc Light.

l	n	n^2	Na—K		Cæsium.	
			d	v	d	v
491.2	6.102	37.25	9.5	0.315	31.4	1.035
227.1	10.84	117.8	57.5	1.91	98.9	3.27
255.8	11.74	138.01	69.8	2.32	116.5	3.84
250.2	11.98	143.81	72.7	2.410	121.3	3.99
213.8	14.05	197.7	105.0	3.485	166.3	5.48
206.4	14.59	212.8	115.8	3.840	180.6	5.92
202.5	14.83	220.1	125.3	4.140	182.0	5.98

The positive potential increases continuously with the frequency, and the geometrical representation of these figures shows that it increases proportionally to the square of the frequency.

It has been found very difficult to prepare the metal with the same photoelectric properties twice in succession. The surface conditions play a very important part in the photoelectric effect; it is, therefore, hardly possible to draw definite conclusions as to the constants of the phenomena. When two samples of cæsium had been prepared under as nearly the same conditions as possible, the positive potentials were quite different for the same light; it might even happen that it was hardly active, and yet the surface appeared perfectly clean.

Though the positive potential increases as the square of the frequency, it was very noticeable that the parabola $v - n^2$ approaches in certain cases the straight line $v - n$, which we should expect from Planck's theory of radiation.

Towards the red end of the spectrum the photoelectric phenomena are different as is seen from the following numbers.

l	d	l	d
520	65.0	640	70.3
540	54.1	660	61.1
560	50.4	680	44.2
580	56.2	700	19.0
600	69.1	720	0.
620	74.2		

l = wave-length, d = deflection.

There is a maximum in the positive potential of sodium potassium alloy at $l = 618$. The positive potential in this region of the spectrum depends on the intensity of the light. Thus the positive potentials have to be expressed as function of the incident energy of radiation. This will be done in the following paper. In these experiments a Nernst glower was used as source of light while for the violet end of the spectrum an ordinary arc was sufficient.

Up to the present time, all measurements indicate that in the violet and ultra-violet region of the spectrum the positive potential in the photoelectric effect is proportional to the square of the frequency and as Roentgen rays may be considered as electromagnetic disturbances of a certain thickness, and as they produce electrons of a high velocity, when incident on a metal plate, we have an experimental basis for determining the thickness of the Roentgen pulse or the wave-length equivalent, as it might conveniently be called, because the pulse in the ordinary primary Roentgen ray has very likely a certain structure, and in the secondary homogeneous Roentgen radiation there may be a certain amount of regular damped oscillation in the pulse. The present method does not allow us to enter into these details of structure, but gives a means of determining from the photoelectric effect the resultant wave-length of the ordinary radiation which would be equivalent to the thickness of the Roentgen pulse.

It has been attempted to measure directly the positive potential excited by Roentgen rays instead of ultra-violet light. But the number of electrons emitted by Roentgen rays is so very small that the potential of the electrode rose very slowly and never reached a definite maximum. It was therefore necessary to measure the maximum velocity of the electrons emitted, rather than the positive potential in the case of equilibrium. The apparatus applied in these experiments is indicated by the following figure.

A brass tube is connected to the vacuum pump so that no light can enter the tube. The Roentgen rays penetrate through a hard-rubber tube *A*, 1.5 mm. thick, into the vacuum where they strike on a plate of zinc *B*. A part of the electrons will pass through two slits, one vertically above the other and make an impression on a photographic plate *D* so that *C*, *D*, *E* are on a straight line, when the magnetic field is not excited. When the tube however is placed between the poles of an electromagnet, the electrons will be deflected and make an impression at *F*. Knowing the distances *CDE* and *EF* and the magnetic field, it is easy to calculate the velocity of the electrons. The hardness of the Roentgen tube is adjusted so that it corresponds to a spark distance of 13 cm. It is necessary to introduce through the palladium from time to time a little hydrogen, in order to maintain the same hardness of the primary beam. The experiment is a very tedious one as it requires over ten hours exposure. The Roentgen tube gets so hot after a short time that the rays can only be produced intermittently; for instance, for five minutes, followed by three minutes rest and so on. As photographic plates I used Seed orthochromatic, a mercury turbine interrupter, and a large Klingelfuss induction coil. The magnetic field was measured by means of a magnetic balance. The photographic plate was cut into strips 5 × 1 cm. For a zinc plate the results of measurements were as follows:

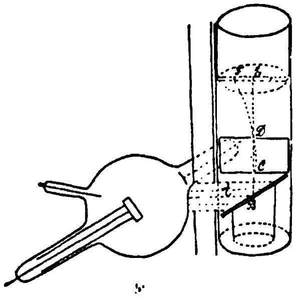

Fig. 2.

$$DC = 2 \text{ cm.} \quad DE = 5 \text{ cm.} \quad EF = 1.40 \text{ cm.}$$

The radius of curvature of the path of the electrons in the magnetic field was equal to:

$r = 13.2$ cm., the magnetic field $H = 28.2$ absolute units.

The value $EF = 1.40$ cm. corresponds to the minimum deflection, or to the maximum velocity of the electrons. The line F on the photographic plate is drawn out somewhat which means that electrons of different velocities are given off. To the positive potential of equilibrium, measured in the previous experiments, corresponds the highest velocity of the electrons or the minimum deflection EF. This velocity is calculated by means of the formula:

$$mv^2/r = Hev, \quad e/m = 1.77. \times 10^7, \quad v = 6.6 \times 10^9, \quad H = 28.3, \quad r = 13.2.$$

This value corresponds well with those determined by P. D. Innes.[1]

For the same plate the positive potential acquired under the action of ultra-violet light was measured and found to be 1.88×10^8 absolute units for $l = 206.4$ mm., $P_2 = 1.88 \times 10^8$, $l_2 = 206.4$, $\mu\mu = 2.064 \times 10^{-5}$ cm. The potential P, corresponding to the velocity $v_1 = 6.6 \times 10^9$, is given by the formula:

$$\tfrac{1}{2}mv_1^2 = P_1e, \quad P_1 = 1.239 \times 10^{12}.$$

Now we find the wave-length equivalent l_1 of Roentgen rays by the following equations, assuming that the curve passes through the origin, which is not correct:

$$P_1 : P_2 = n_1^2 : n_2^2, \quad n_1/n_2 = l_2/l_1 = \sqrt{P_1/P_2},$$
$$L_1 = 2.65 \times 10^{-7} \text{ cm.}$$

This would be the wave-length equivalent of those Roentgen rays which have been studied. The value determined by this principle of the photoelectric effect is large compared with those which have been estimated from other phenomena. The determination has been repeated with a lead plate instead of zinc, and with nearly the same result.

The measurements will be extended to other metals. It is hoped also that the principle here applied may be used for the determination of the wave-length equivalent of γ-rays and of secondary Roentgen radiation. The wave-length equivalent and the thickness of the pulse of Roentgen rays according to the electromagnetic theory must depend on the velocity of the primary cathode particles, and the study of the relations between the velocities of the primary and secondary electrons will throw some light on the forces that come into play in the collision between an electron and an atom.

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[1] P. D. Innes, On the Velocity of the Cathode Particles, Proceedings of the Royal Society of London, 79, p. 442, 1907.

The wave-length equivalent l of Roentgen rays is equal to ct, where c is the velocity of light and t the time of collision between an electron and an atom. In the electron theory of radiation we assume, that the time of collision t is inversely proportional to the square of the velocity of the electron, $t = c_1/v^2$. If the radiation of the black body and the Roentgen rays are intimately related phenomena, then we conclude that:

$$\tfrac{1}{2} mv^2 = Pe; \quad t = c_3/P; \quad l = c_4/P.$$

Thus the wave-length equivalent of Roentgen rays would be inversely proportional to the potential difference between the cathode and anode. This last relation is susceptible of an experimental verification.

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June 16, 1911.

NOTE ON A VARIABLE LOW RESISTANCE.

By J. H. Dellinger.

THERE is at present a tendency in electrical measurements to increase the precision of measurement of low resistances, inductances and electromotive forces by the use of low resistances in the bridge arms or in the potentiometer circuit. Such work requires a convenient low resistance, of small total resistance, capable of definite variation in practical cases of steps as small as one millionth of an ohm, which introduces no irregular variable resistance. Observers are so frequently troubled by the ordinary variable contacts that it seems worth while to point out the advantages of a simple device which anyone may construct for himself, viz., an amalgamated copper wire plunging in a tube of mercury. It is not known that a description of this device has been published, although the idea has been used in various forms by many experimenters. In the device here described the copper wire is used to short circuit the mercury, the operation depending on the fact that mercury has approximately 60 times the resistivity of copper. This principle has a notable advantage in alternating current work, which will be explained below.

The apparatus consists simply of a tube of thin glass (thick glass may be broken by scratching of the copper wire), or of porcelain or hard rubber, with a slight enlargement at the upper end to receive the mercury when displaced by the descending copper wire. An amalgamated copper wire, of slightly smaller diameter than the internal diameter of the tube, is lightly gripped either by a cork placed in the top of the tube, or by a pair of springs faced with insulating material. A length of 15 cm. is convenient. A 1-ohm range is obtained by using a tube of about 0.4 mm. diameter, and any other range down to 0.01 ohm. is obtained by tubes up to 4 mm. diameter. In the first of these mercury variable resistances, a flexible lead wire was connected to the upper end of the copper wire, and to prevent opening the circuit when the wire was wholly withdrawn from the mercury a wire shunt was connected across the terminals. An improvement in the connections was suggested by Dr. F. Wenner, viz., to connect simply to the top and bottom of the mercury column. Thus there is nothing whatever connected to the plunging copper wire, which functions simply by shortcircuiting the mercury. A simple and valuable modification is the use of two of these resistances in series by the employment of a glass U-tube of which the diameter of one leg is $\sqrt{10}$ times the other. Thus a pair of variables of the ranges 0.1 ohm. and 0.01 ohm are conveniently obtained. The use of the U-tube eliminates the difficulty of sealing the lower end. A scale may readily be attached, and when the instrument has been calibrated the resistances of its settings are known. The instrument should not usually be used for exact quantitative work, however, as it has a large temperature coefficient.

The mercury variable resistance has been applied to facilitate adjusting to a balance the auxiliary ratio arms of the Thomson bridge, in the comparison of low resistance standards, and its use materially increases the speed of working. It is especially valuable in the measurement of the resistance of wire samples for determination of the conductivity, since the magnitude of the ratio arms may be very different for every sample measured. It has also been found to be a convenience in the comparison of mercury ohms with wire standard ohms, since the potential leads of the mercury standards are of relatively high resistance with respect to the ratio arms. This apparatus has also been usefully applied to the regulation of potentiometer currents.

The application of this device to alternating current bridge work has been productive of good results. The precision of determination of low inductances may be increased by the use of ratio arms of lower resistance. This has been made convenient by the use of the mercury variable resistance. It was found that, fortunately for alternating current work, this variable resistance has practically non-variable inductance (at any rate for moderate frequencies). This is evident, if the copper wire is of practically the same diameter as the mercury column, as the geometry of the circuit is not changed by varying the resistance. Thus this instrument is a complementary apparatus to the usual variable inductance. The total change of inductance of one of these "mercury variables" 15 cm. long, about 1.5 mm. internal diameter of tube, 1 mm. diameter of copper wire, and a range of 0.05 ohm, was $6\ (10)^{-9}$ henry, or 6 centimeters.

BUREAU OF STANDARDS,
WASHINGTON, April 28, 1911.

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THE

PHYSICAL REVIEW.

SOME THERMODYNAMIC PROPERTIES OF AIR AND OF CARBON DIOXIDE.

By A. G. Worthing.

I. Introduction.

GAY-LUSSAC[1] was the first to investigate the question as to whether or not the internal energy of a mass of gas is a function of its volume. He was not able to conclude that the internal energy was a function of the volume. On Gay-Lussac's work R. Mayer[2] based his computations for the mechanical equivalent of heat. Joule[3] with somewhat greater care and with a modified method came to the same conclusion. In each of these experiments, the gas under consideration was allowed to expand freely, that is without the performance of external work and without the addition or subtraction of heat. This latter condition was only imperfectly realized. The question as to whether or not the internal energy of the gas was a function of the volume depended directly on whether or not the freely expanding mass of gas taken as a whole suffered any change in temperature. The ratio of such a change in temperature to the change in pressure for small changes in pressure is called the free-expansion effect. Later repetitions of Joule's experiment by Regnault[5] and by Hirn[6] led to the same result. Cazin[7] about 1870 sought to do away with errors due to heating. He noted the variations with time of a fluctuating liquid pressure gauge one side of which was connected to the chamber containing the gas under experimentation. Cazin concluded that the internal energy of a gas was a function of its volume and obtained values therefor which will be noted later. Due to the use of extended extrapolations and the presence of heating effects in the stop-cock separating his two chambers initially, the results are of doubtful significance. The writer is in receipt of a letter from Professor R. A. Millikan, in which he states that he has tried a method differing from Cazin's in that the fluctuations of the liquid in the pressure gauge were eliminated by a null method. He was not able, however, to eliminate the heating effects at the stop-cock.

The method first successfully employed was due to Joule and Thomson[9] (Lord Kelvin). Their celebrated porous plug experiments gave consistent results, which only needed corrections for external work done by the gas in the expansion in order to show the dependency of the internal energy of the gas upon the volume. The physical quantity (μ) determined by them was the ratio of the change in temperature to the change in pressure for small changes of pressures occurring as the gas passed through the porous plug. This quantity has since received the name Joule-Thomson effect or Joule-Kelvin effect. For moderate pressures they found μ independent of the pressure and dependent on the temperature as shown in (1),

$$(1) \qquad \mu = A/\theta^2.$$

Rose-Innes,[10] D. Berthelot[11] and Buckingham[12] have given other equations for representing the same effect.

Natanson,[13] working with CO_2 under higher pressures, found a noticeable though small diminution in the Joule-Kelvin effect for increased pressures. Kester,[14] working with CO_2 under still greater pressures, did not find this change due to the change in pressure. Rudge[15] has recently made some rough determinations for CO_2 with a modified method, in which the gas escapes from a pierced bulb in a calorimeter, through a long piece of narrow tubing. His results as a whole are in agreement with those of the previous experiments mentioned. Recently Dalton,[16] working with air, has found an effect similar to that found by Natanson for CO_2. Witkowski,[17] having in view the applications to liquid air machines, applied thermodynamic formulæ to a great many experimentally determined results. He computed by graphical methods a series of curves which were drawn on a pressure-temperature diagram, the slopes of which at any point give directly for that point the Joule-Kelvin and the free-expansion effects. Many steps are involved in reaching the final results, and confirmation is needed for this highly important work. Searle,[8] making use of Van der Waal's equation and assuming the constancy of the isometric heat capacity, computed for CO_2 the change in temperature for the gas expanding from a pressure of 10 atmos. to 5 atmos. Some of the results of these investigations will be noted later.

The present paper is the immediate outcome of an attempt to better comprehend the dependency of the ratio of the two heat capacities of a substance γ on its pressure and temperature. It has led to the development of a certain thermodynamical equation which relates the ratio γ to the free-expansion effect. This together with another well-known relation for the Joule-Kelvin effect has been used in computing these effects for air and CO_2. There existed what seemed to be satisfactory data for air. An experimental study of γ for CO_2 was undertaken in this connection to complete what seemed necessary data for that gas.

II. Derivation of Formulæ Relating the Ratio γ to the Free-Expansion and the Joule-Kelvin Effects.

For convenience there is given in Table I. the symbols and the units of some of the quantities used in this discussion.

Definitions of N. V. Unit, T. N. V. Unit, μ *and* η.—The "normal volume unit" (N. V. unit) of a substance is defined by K. Onnes[25] as the volume actually occupied at 0° C. by one gram-molecule of the substance when under a pressure of one atmosphere. The "theoretical normal volume unit" (T. N. V. unit) is defined as the volume that would

Table I.

Symbols and units of some of the quantities used.

Quantity.	Symbol.	Unit.
Pressure,	p	atmosphere.
Specific volume,	v	$\frac{\text{N. V. unit}}{\text{gr. mol.}}, \frac{\text{T. N. V. unit}}{\text{gr. mol.}}$.
Temperature,	T	degree Centigrade.
Thermodynamic temperature,	θ	degree Kelvin.
Time,	t	second.
Reduced pressure,	π	critical pressure.
Reduced temperature,	τ	critical temperature.
Reduced specific volume,	ν	critical specific volume.
Quantity of heat,	Q	atmo. × N. V. unit.
Specific internal energy,	ϵ	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.}}$.
Isopiestic heat capacity,	C_p	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}, \frac{\text{calories}}{\text{gr.} \times \text{deg.}}$.
Isometric heat capacity,	C_v	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}, \frac{\text{calories}}{\text{gr.} \times \text{deg.}}$.
Ratio of the two heat capacities,	γ	
Internal work in infinitesimal, reversible, isothermal expansions,	ΔW_1	atmo. × N. V. unit.
External work in infinitesimal, reversible, isothermal expansions,	ΔW_2	atmo. × N. V. unit.
Free-expansion effect,	η	$\frac{\text{deg.}}{\text{atmo.}}$.
Joule-Kelvin effect,	μ	$\frac{\text{deg.}}{\text{atmo.}}$.

be occupied at 0° C. by one gram-molecule of the substance under a pressure of 1 atmosphere if the gas obeyed Boyle's Law. It is assumed that the value of the product pv in such a case is the value of pv which may be obtained by extrapolation to zero pressure when considering the behavior of the actual gas. The measuring of volume in such units requires that C_p, C_v and ϵ be expressed in the units given in Table I. instead of the common units of cal./(gr. × deg.) and cal./gram. The free-expansion effect, η, of a substance, as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance into a vacuum. Mathematically it is

$$\eta = (\partial\theta/\partial p)_{\epsilon}. \tag{2}$$

The Joule-Kelvin effect, μ, as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance through an orifice or a porous plug from one maintained pressure to another maintained pressure. Mathematically it is

$$\mu = (\partial\theta/\partial p)_{\epsilon+pv}. \tag{3}$$

For the sake of accuracy in the theoretical discussions, it has been necessary to express temperature in the units of the thermodynamic scale. For other purposes it makes but little difference in the present work whether temperatures are measured in this scale or in the more common centigrade scale. In the adapting of experimental data, the writer has assumed that the degree Kelvin and the degree centigrade were equal.

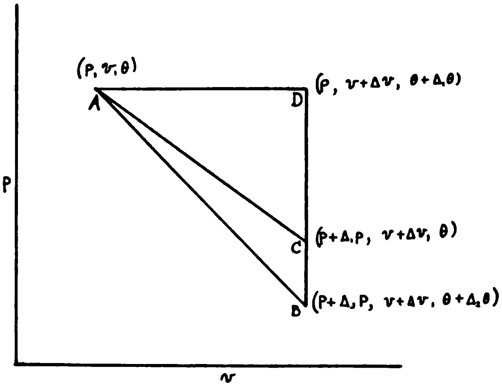


Fig. 1.

Derivation of Equation Relating η and γ.—The equation relating η, the free-expansion effect, to γ, the ratio of the two heat capacities may be readily obtained. Consider hanges in ϵ, the internal energy of the substance under consideration, for transformations indicated in Fig. 1. Let the change represented by the straight line AB be an infinitesimal transformation in which there is no change in the specific internal energy ϵ, an infinitesimal free-expansion. Let the changes represented by AD, DB and AC be respectively infinitesimal isopiestic, isometric and isothermal transformations. Due to carrying the substance around the cycle $ABDA$, no resultant change occurs in ϵ. Consequently the individual changes in ϵ occurring in the individual transformation making up the cycle must sum up to zero. Moreover, since there are no changes in ϵ along AB, the changes in ϵ in passing along BD and DA must sum up to zero. Hence

$$C_v(\Delta_1\theta - \Delta_2\theta) - C_p\Delta_1\theta + p\Delta v = 0. \tag{4}$$

Since the transformations are infinitesimal, we have

$$\Delta_1\theta = \frac{\Delta_1\theta}{\Delta v}\Delta v = \left(\frac{\partial\theta}{\partial v}\right)_p \Delta v, \tag{5}$$

and

$$\Delta_2\theta = \frac{\Delta_2\theta}{\Delta_2 p}\frac{\Delta_2 p}{\Delta v}\Delta v = \left(\frac{\partial\theta}{\partial p}\right)_\epsilon \left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta_v. \tag{6}$$

$$= \eta\left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta v.$$

Eliminating $\Delta_1\theta$, $\Delta_2\theta$ and Δv from (4), we have

$$(C_p - C_v)\left(\frac{\partial\theta}{\partial v}\right)_p - p + \eta C_v\left(\frac{\partial p}{\partial v}\right)_\epsilon = 0. \tag{7}$$

An expression for $(\partial p/\partial v)_\epsilon$ may be obtained as follows. For all transformations we have

$$dp = \left(\frac{\partial p}{\partial\theta}\right)_v d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta dv. \tag{8}$$

Hence

$$1 = \left(\frac{\partial p}{\partial\theta}\right)_v \frac{d\theta}{dp} + \left(\frac{\partial p}{\partial v}\right)_\theta \frac{dv}{dp}. \tag{9}$$

For a free-expansion (9) becomes

$$1 = \left(\frac{\partial p}{\partial\theta}\right)_v \left(\frac{\partial\theta}{\partial p}\right)_\epsilon + \left(\frac{\partial p}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial p}\right)_\epsilon, \tag{10}$$

or

$$\left(\frac{\partial p}{\partial v}\right)_\epsilon = \frac{\left(\frac{\partial p}{\partial v}\right)_\theta}{1 - \eta\left(\frac{\partial p}{\partial\theta}\right)_v}. \tag{11}$$

The elimination of $(\partial p/\partial v)_t$ from (7) and (11) gives

$$(12)\qquad \gamma = \frac{C_p}{C_v} = 1 + \frac{p}{C_v}\left(\frac{\partial v}{\partial \theta}\right)_p + \frac{\eta\left(\frac{\partial p}{\partial \theta}\right)_v}{1 - \eta\left(\frac{\partial p}{\partial \theta}\right)_v}.$$

The expressions for γ usually derived in text-books on physics are equivalent to the first two terms of the right-hand member of (12). By means of it and of certain assumptions regarding the application of the kinetic theory of gases, it is shown that for cases where such assumptions are realized the limiting values of γ are 1 and $1\frac{2}{3}$. Equation (12), however, is a perfectly general expression. It reduces to the more common expression for small pressures where $(\partial p/\partial \theta)_v$ is small and the term containing η may be disregarded. The writer has not seen elsewhere any expression similar to (12).

Equation (12), when combined with the following well-known relation deduced in texts on thermodynamics

$$(13)\qquad C_p - C_v = \theta\left(\frac{\partial p}{\partial \theta}\right)_v\left(\frac{\partial v}{\partial \theta}\right)_p,$$

gives

$$(14)\qquad \eta = \frac{\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p}{\frac{\gamma}{\gamma - 1}\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p}\left(\frac{\partial \theta}{\partial p}\right)_v.$$

Expression of μ as a function of γ.—In texts on thermodynamics the following equation for the Joule-Kelvin effect is derived:

$$(15)\qquad \mu = \frac{\theta\left(\frac{\partial v}{\partial \theta}\right)_p - v}{C_p}.$$

Equations (13) and (15) lead directly to the following

$$(16)\qquad \mu = \frac{\gamma - 1}{\gamma}\,\frac{\theta - v\left(\frac{\partial \theta}{\vartheta v}\right)_p^{]}}{\theta\left(\frac{\partial p}{\partial \theta}\right)_v}.$$

Equations (14) and (16) are the two relations, the application of which form certain of the main subdivisions of this paper.

III. THE FREE-EXPANSION AND JOULE-KELVIN EFFECTS IN AIR.

Inspection of Available Data.—In order to apply equations (14) and (16), there are needed experimental data regarding γ, the interrelations of p, v, θ and their partial derivatives $(\partial p/\partial\theta)_v$ and $(\partial v/\partial\theta)_p$. γ for air may be obtained from data by Witkowski,[26] by Koch,[24] or from data by Joly[27] and Lussana.[28] Witkowski first computed C_p and C_v and then γ. C_p was obtained from the relation

$$(17)\qquad \left(\frac{\partial C_p}{\partial p}\right)_\theta = -\theta\left(\frac{\partial^2 v}{\partial\theta^2}\right)_p .$$

C_v was obtained by means of (13). Values of γ were then computed for various temperatures ranging from 0° C. to −140° C., and for pressures up to about 130 atmospheres. Later by Kundt's velocity of sound method, he measured γ directly under pressures up to 100 atmospheres and at 0° C. and −78.5° C. These results, though noticeably higher, agree quite well with the computed results, as may be seen by an inspection of Table II. Koch's results were likewise obtained by Kundt's velocity of sound method. In his experiments the pressure varied from 1 to 200 atmospheres. The temperatures were 0° C. and −79.3° C. His results agree well with Witkowski's. Joly determined C_v for air by means of his well-known, differential, steam-calorimeter method for various temperature intervals all above 0° C. and for pressures up to about 100 atmospheres. Average values of C_p for air were determined by Lussana for various intervals of temperature between 0° C. and 200° C. and for various pressures up to 100 atmospheres. These values of C_v and C_p and the values of $(\partial v/\partial\theta)_p$ and $(\partial p/\partial\theta)_v$ obtained by Amagat from his experiments on the compressibility of air, have been shown by Amagat to be quite inconsistent with one another. Data by Joly and Lussana have therefore not been relied upon in this work. The writer has seen only an abstract of Witkowski's paper in which the Kundt method of measuring γ was detailed. For the above reasons and for the added reason that the data by Koch seemed to have been obtained with great care, Koch's data have been used in the following computations. The values obtained from Koch's paper are to be found in Table II., column 7.

For the determination of the interrelations of p, v, and θ and the partial derivatives $(\partial v/\partial\theta)_p$ and $(\partial p/\partial\theta)_v$, there exist the works of Amagat,[29] Witkowski[17] and Koch[24]. Amagat's data relate to temperatures above 0° C. and can not be used in connection with the data on γ selected. Witkowski's results on the compressibility of air cover the range of temperatures and pressures of the γ data selected. Moreover, the values of the product pv as a function of p at 0° C. and − 78.5° C. have been fairly well verified by Koch. Witkowski's data on the compressibility of air have therefore been made use of.

Method of Handling p, v, θ data.—In applying equations (14) and (16), $(\partial v/\partial\theta)_p$ and $(\partial p/\partial\theta)_v$ do not merely appear by themselves but also in the expressions $v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v$. The values for these expressions were obtained as follows: Consider

$$(pv)_\theta = f(p). \tag{18}$$

The derivation of (18) with respect to p gives on rearranging

$$\left(\frac{\partial p}{\partial v}\right)_\theta = -\frac{p}{v - f'(p)}. \tag{19}$$

Likewise we may consider

$$(v)_p = F(\theta). \tag{20}$$

Whence

$$\left(\frac{\partial v}{\partial \theta}\right)_p = F'(\theta), \tag{21}$$

and

$$v\left(\frac{\partial \theta}{\partial v}\right)_p = \frac{F(\theta)}{F'(\theta)}. \tag{22}$$

Since

$$\left(\frac{\partial p}{\partial \theta}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial \theta}\right)_p, \tag{23}$$

$$\theta\left(\frac{\partial p}{\partial \theta}\right)_v = \frac{p\theta F'(\theta)}{v - f'(p)}. \tag{24}$$

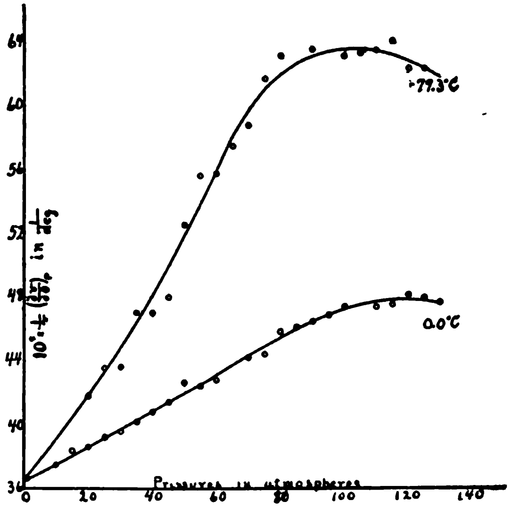


Fig. 2.

Variation of $\frac{1}{v}\left(\frac{\delta v}{\delta \theta}\right)_p$ with pressure for air.

For air at various pressures and at 0° C. and − 79.3° C., $f'(p)$ and $F'(\theta)$ were obtained from Witkowski's data by graphical means. The individual values of the reciprocals of $v(\partial\theta/\partial v)_p$ which were obtained together with the smoothed curves are shown in Fig. 2. The values used were taken from these curves.

Results from Data by Witkowski and Koch.—Certain data and computations leading to the values of μ and η are included in Table II. The

Table II.

Computations for μ and η of air using data obtained by Witkowski and by Koch. Air at 0° C.

p	pv	$\log\left[-\left(\frac{\partial p}{\partial v}\right)_\theta\right]$	$\log\left(\frac{\partial v}{\partial \theta}\right)_p$	$\theta - v\left(\frac{\partial \theta}{\partial v}\right)_p$	$\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p$	γ	μ	η	$\frac{\Delta W_1}{\Delta W_2}$
10	.9951	1.9997	$\bar{4}.5737$	7.7	.23	1.435	.228	.259	.023
15	.9923	2.3519	.4026	11.4	.52	1.448	.227	.260	.035
20	.9897	2.6017	.2824	15.0	.92	1.460	.226	.259	.046
25	.9869	2.7958	.1906	18.6	1.48	1.472	.225	.265	.059
30	.9842	2.9546	.1160	22.0	2.13	1.483	.223	.263	.071
40	.9793	3.2057	.0005	28.7	3.92	1.508	.220	.270	.090
50	.9754	3.4010	$\bar{5}.9134$	35.1	6.35	1.533	.217	.275	.127
60	.9723	3.5614	.8440	41.2	9.48	1.557	.212	.278	.158
70	.9701	3.6969	.7881	47.0	13.46	1.582	.207	.281	.192
80	.9688	3.8160	.7392	52.5	18.10	1.603	.201	.279	.226
90	.9681	3.9212	.6984	57.7	23.8	1.625	.195	.278	.264
100	.9681	4.0155	.6598	61.3	29.4	1.645	.186	.270	.294
110	.9690	4.1034	.6244	64.0	36.0	1.663	.175	.263	.327
120	.9710	4.1838	.5882	64.5	41.6	1.682	.162	.253	.347
130	.9738	4.2602	.5530	63.6	47.7	1.700	.147	.243	.367
Air at −79.3° C.									
1	.708	.1488	$\bar{3}.5643$	.8		1.405	.230		
10	.690	2.1500	$\bar{4}.5866$	15.1	.57	1.463	.452	.447	.057
15	.681	2.5022	.4236	22.6	1.34	1.495	.458	.463	.089
20	.672	2.7520	.3124	30.1	2.48	1.530	.464	.476	.124
25	.664	2.9459	.2299	37.4	4.05	1.567	.466	.489	.162
30	.655	3.1046	.1644	44.3	6.01	1.602	.462	.492	.200
40	.638	3.3541	.0664	56.9	11.04	1.681	.452	.487	.276
50	.620	3.5483	.0062	71.6	19.48	1.765	.447	.493	.390
60	.606	3.7071	$\bar{5}.9554$	81.9	29.01	1.857	.424	.474	.483
70	.587	3.8499	.9209	93.1	44.4	1.950	.397	.457	.634
80	.573	3.9819	.8783	99.0	60.5	2.044	.360	.431	.756
90	.562	4.0981	.8340	102.3	75.8	2.125	.327	.397	.842
100	.554	4.2097	.7900	104.0	93.7	2.200	.293	.368	.937
110	.550	4.3122	.7478	104.4	112.5	2.290	.264	.344	1.023
120	.547	4.3998	.7072	104.3	128.0	2.370	.243	.324	1.067
130	.546	4.4804	.6683	103.7	143.0	2.460	.226	.308	1.100

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, and μ and η in $\frac{\text{deg.}}{\text{atmo.}}$.

value of the ice point for this table was taken as 273.2° K. The value used for the other and later computation was 273.1° K. The variations produced by not using the latter value throughout are inappreciable, hence Table II. has not been corrected in this respect. The computed free-expansion and Joule-Kelvin effects are indicated in Fig. 3 by open circles.

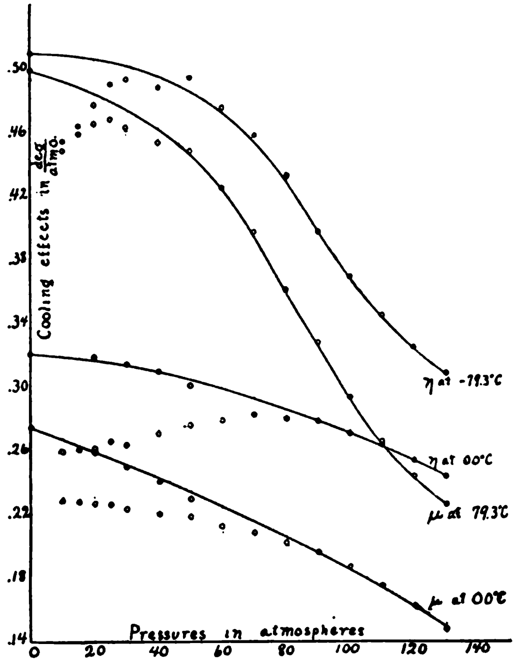


Fig. 3.

Variation with pressure of the free-expansion (η) and Joule-Kelvin (μ) effects in air at 0.0° C. and - 79.3° C.

Results based on

Witkowski's data .... ○

K. Onnes's equation .... ●

K. Onnes's Equation.—The values in Fig. 3 indicated by circles with filled centers are obtained by using Kamerlingh Onnes's[16] empirical equation representing the isothermals of air at 0° C., 20° C. and 99.4° C. for pressures up to about 50 atmospheres and Koch's data on γ. The equation given by Kamerlingh Onnes is

$$pv = A + \frac{B}{v} + \frac{C}{v^2}, \tag{25}$$

where v is expressed in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, p in atmospheres, and A, B and C

are functions of θ, the individual values of A, B and C are as shown for the given temperatures in Table III.

TABLE III.

Constants for Kammerlingh Onnes's empirical equation for air.

T	A	B	C
0.0° C.	1.0006	$-.0_{3}57440$	$.0_{5}29594$
20.0° C.	1.0739	$-$ 40495	30178
99.4° C.	1.3647	$+$ 25057	35669

Results from K. Onnes's Equation and Koch's Data.—The computations for μ and η, excepting those for zero pressure, differ in this case from those in which the p, v, θ relations were obtained from Witkowski's data in that $(\partial p/\partial v)_\theta$ was obtained in this case by differentiation. Table IV. indicates these results.

TABLE IV.

Computations for μ and η of air at 0° C. using Kammerlingh Onnes's equation of state and γ data by Koch.

p	pv	$\log\left[-\left(\frac{\partial p}{\partial v}\right)_\theta\right]$	$\log\left(\frac{\partial v}{\partial \theta}\right)_p$	$\theta - v\left(\frac{\partial \theta}{\partial v}\right)_p$	$\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p$	γ	μ	η	$\frac{\Delta W_1}{\Delta W_2}$
0	1.0006	——	——	——	——	——	.273	.320	.000
10	.9952	2.0000	$\bar{4}.5759$	8.9	.29	1.435	.262	.322	.029
20	.9902	2.6022	.2869	17.3	1.16	1.448	.258	.318	.058
30	.9859	2.9550	.1220	24.9	2.62	1.460	.249	.313	.087
40	.9822	3.2060	.0073	31.7	4.64	1.472	.239	.308	.116
50	.9790	3.4009	$\bar{5}.9199$	37.7	7.18	1.483	.229	.300	.144

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, and μ and η in $\frac{\text{deg.}}{\text{atmo.}}$.

Values for μ and η at Zero Pressure.—The values for μ_0 and η_0 at $p = 0$ were obtained by a method indicated for μ_0 by J. P. Dalton.[16] The method of obtaining η_0 is outlined briefly here. By means of (13), (14) may be rewritten as

$$\eta = \frac{\theta - p\left(\frac{\partial \theta}{\partial p}\right)_v}{C_p\left(\frac{\partial \theta}{\partial v}\right)_p - p}. \tag{26}$$

By the direct processes of calculus and by the substitution of $v = \infty$, we get

$$\eta_0 = \frac{1}{C_{p0} - \frac{\partial A}{\partial \theta}} \frac{\theta\left(\frac{\partial B}{\partial \theta}\right) - B}{A}. \tag{27}$$

The analogous value for μ_0 obtained from (15) is

$$\mu_0 = \frac{\theta \frac{\partial B}{\partial \theta} - 2B}{C_{p0} A}. \tag{28}$$

The well established value of C_{p_0} for air under low pressures is very closely $.2375 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$, or in the units consistent with those chosen for p and v in this paper $.01273 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.} \times \text{deg.}}$.

It is to be noticed that the two sets of values for μ and η included in Tables II. and IV. differ considerably, the greatest variations occurring with the smaller pressures. This is evidently due to the smallness of the quantities $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$. The entire differences result from very small but noticeable variations in corresponding values of $(\partial v/\partial\theta)_p$. This source of uncertainty is plainly much less effective at the higher pressures.

Results for μ at 0° C.—The value obtained for the Joule-Kelvin effect at zero pressure μ_0 at 0° C. from Kamerlingh Onnes's equation agrees very closely, as has been shown by J. P. Dalton, with the experimental value obtained by Joule and Kelvin and with his own experimental value. It also agrees very well with the computed value obtained by using Buckingham's equation in which he expressed in a single formula the results of all experimental Joule-Kelvin effects for various substances under moderate pressures, as a function of the temperature. Each of these values closely approximates $.273 \frac{\text{deg.}}{\text{atmo.}}$. This value has therefore been selected on the plot Fig. 3, as the starting point for the curve at 0° C. J. P. Dalton's experimental results for the porous plug expansion of air through a glass reduction-valve are very well represented by the equation,

$$T_1 - T_2 = .273(p_1 - 1) - .000208(p_1^2 - 1). \tag{29}$$

p_1 represents the initial pressure of the air, a quantity which in his experiments reached a pressure of 43 atmospheres. T_1 the initial temperature was 0° C. The final pressure was that of the atmosphere. T_2 represents the final temperature. The ratio $\frac{T_1 - T_2}{p_1 - 1}$, if platted on Fig. 2 would start with the same initial value for μ_0 as chosen and would continue from there in a line lying approximately half way between the line $\mu = .273 \frac{\text{atmo.}}{\text{deg.}}$ and a line passing through the points determined by

Kamerlingh Onnes's equation and the γ data of Koch. When it is remembered that the results of Dalton represent effects from finite expansion of considerable magnitude and that the mean temperatures during such expansions are, for the higher pressures especially, noticeably less than 0° C., for which temperatures the Joule-Kelvin effect becomes greater, it will be seen that the deviation spoken of above is to be expected. Moreover, it may be readily shown that this deviation agrees in magnitude with what is obtained by some rather rough computations. For an initial pressure of 40 atmospheres, (29) gives for T_2 a value of $-10.3°$ C. If now (1) may be taken as approximately true, and if it is further assumed that the value of μ for 0° C. and atmospheric pressure is $.273 \frac{\text{deg.}}{\text{atmo.}}$, it follows that the value of μ for $-10.3°$ C. and atmospheric pressure is $.294 \frac{\text{deg.}}{\text{atmo.}}$. The value for μ at 0° C. and 40 atmospheres, according to data based on Kamerlingh Onnes's equation, is $.239 \frac{\text{deg.}}{\text{atmo.}}$. For air initially at 0° C. and 40 atmospheres, expanding through a valve as in J. P. Dalton's experiment to atmospheric pressure, an average value for μ might be expected which is near the mean of the extreme values given above. This computed average for μ, $.266 \frac{\text{deg.}}{\text{atmo.}}$, agrees very well with the value to be obtained from (29), $.264 \frac{\text{deg.}}{\text{atmo.}}$. Because of these agreements, it has been assumed in drawing the curve for μ at 0° C. that the values computed with the aid of Kamerlingh Onnes's equation of state are correct. The general trend of these values are such as to show agreement with the values of μ obtained for the higher pressures using Witkowski's data. It might be expected that these latter values would not be far from the correct values, since here, as may be seen in Table II., small errors entering into $\theta - v(\partial\theta/\partial v)_p$ would cause but small errors in the computed results for μ. Hence the further continuance of the curve. The curve for μ at 0° C. is well represented by (30).

$$(30) \qquad \mu_{T=0} = .273 - .00076p - .0000012p^2.$$

Results for μ at $-79.3°$ C.—In drawing the curve for μ at $-79.3°$ C., the value given by Buckingham's equation was selected as being the most probable value for μ at zero pressure. This value of $.498 \frac{\text{deg.}}{\text{atmo.}}$ was found to agree very well with the value $.486 \frac{\text{deg.}}{\text{atmo.}}$ for $-78.5°$

which was obtained by using as before, equations similar to (25) and Witkowski's experimental value of C_p .2375 $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ or .01273 $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$. The equations used here however were of the type

$$pv = A + B/v. \tag{31}$$

A and B have the values indicated in Table V. at the stated temperatures

TABLE V.

Constants for equation (31).

T	A	B
0.0° C.	1.0006	−.000574
− 78.5	.7130	−.001193
−103.5	.6214	−.001473

when as before p is expressed in atmospheres and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$. The values of A and B relating to 0° C. have been given by Kamerlingh Onnes. The remaining values of A were determined on the supposition that at zero pressure air rigorously obeys the perfect gas law. The remaining values for B were determined with the additional supposition that Witkowski's data on the values of v for air at − 78.5° C. and − 103.5° C. for a pressure of 20 atmospheres are correct. These values are respectively .03389 and .02848 $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$.

Results for η at 0° C.—In drawing the curve for the free-expansion effect η of air at 0° C., preference was given at small pressures to the values computed with the aid of Kamerlingh Onnes's equation and constants, because they had given very nearly the correct results for the Joule-Kelvin effect at the same temperature and pressure. It is, of course, to be borne in mind that, even if an equation of state should indicate correct values for the Joule-Kelvin effect for any pressure and temperature, the computed free-expansion effects as determined by that equation of state might deviate far from the true values. If, however, in addition to leading to the correct Joule-Kelvin effects, the equation correctly represents the isothermals, then as has been shown by Bakker,[30] the equation will lead to correct free-expansion effects. As in connection with the Joule-Kelvin effect and for a similar reason, we may expect that the computed free-expansion effects based on Witkowski's data, in the case of high pressures, will not deviate far from the true values.

Here $\theta(\partial p/\partial \theta)_v - p$ is the term which practically determines the accuracy of the computed results. The writer knows of no direct determinations of η which might be used here. The curve for η at 0° C. is well represented by (32).

$$(32) \qquad \eta_{T=0} = .320 - .00018p - .0000032p^2.$$

Results for η at $-79.3°$ C.—In drawing the curve for the free-expansion effect η at $-79.3°$ C., the value for zero pressure was chosen as follows: The value computed with the aid of equation (31) and the accompanying constants for zero pressure and $-78.5°$ C. was $.496 \frac{\text{deg.}}{\text{atmo.}}$. Since the Joule-Kelvin effect for zero pressure and $-78.5°$ C. computed from the same data differed by $.012 \frac{\text{deg.}}{\text{atmo.}}$ from the value given by Buckingham's equation for $-79.3°$ C., and since the variations of μ and η with temperature seem to be about the same, as the general trend of the curves drawn indicate, it was assumed, that the value for η_0 at $-79.3°$ C. was higher than the computed value at $-78.5°$ C. by $.012 \frac{\text{deg.}}{\text{atmo.}}$, making the value selected $.508 \frac{\text{deg.}}{\text{atmo.}}$.

Agreement with Witkowski's Results.—There has been mentioned the work of Witkowski.[17] He started with a number of experimentally determined relations between p, v and θ, and with the experimental conclusion that C_p for air at 1 atmosphere is independent of the temperature, computed isenthalpic and isenergic curves for air embracing a region from 0° C. to $-140°$ C. and from zero pressure to 130 atmospheres. Graphical methods were largely used. The slopes of these curves give directly the Joule-Kelvin and the free-expansion effects. The writer has included in Table VI. a number of values for μ and η thus obtained together with the corresponding values from the present work. Excepting for the lower pressures, the agreement is good. As has been previously suggested, the variations here are undoubtedly largely due to the smallness of the corresponding values for $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$. Witkowski himself ascribed the variation of his results from those of Joule and Kelvin to the uncertainties entering into his graphical calculations.

Internal Work of Expansion.—It is of considerable interest in this connection to consider the relative magnitudes of the effects of the internal forces, intramolecular as well as intermolecular, which give rise to the free-expansion and to a large extent to the Joule-Kelvin effects. This

TABLE VI.

Corresponding values of μ and η according to Witkowski and to Worthing.

T in °C.	Values of μ in $\frac{\text{deg.}}{\text{atmo.}}$			T in °C.	Values of η in $\frac{\text{deg.}}{\text{atmo.}}$		
	p in Atmos.	(Witkowski.)	(Worthing.)		p in Atmos.	(Witkowski.)	(Worthing.)
0.0	40	.20	.242	0.0	50	.23	.303
	70	.23	.215		84	.265	.282
	113	.175	.175		121	.252	.252
−79.3	0	.515	.498	−79.3	19	.491	.505
	15	.496	.490		38	.509	.496
	30	.476	.476		55	.500	.480
	43	.468	.460		71	.468	.452
	57	.448	.430		88	.424	.403
	69	.400	.397		104	.358	.358
	83	.365	.349		122	.323	.322
	97	.308	.303				
	112	.248	.260				
	130	.222	.226				

may best be done by determining the ratio of the work done against these internal forces ΔW_1 to that done against external forces ΔW_2 when a gas undergoes an infinitesimal, reversible, isothermal expansion. The internal work for such an expansion is evidently equal to the change in internal energy, which in turn is equal to the heat, measured in appropriate units, which must be added to the substance following the free-expansion from the initial to the final volume to bring it without changing the volume to the initial temperature.

$$(33) \qquad \Delta W_1 = (\Delta\epsilon)_\theta = - C_v\eta(\Delta p)_\epsilon = - C_v\eta\left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta v.$$

With the aid of (11), (12) and (13), there follows

$$(34) \quad \Delta W_1 = \left(\frac{\partial\epsilon}{\partial v}\right)_\theta \Delta v = - \frac{C_v\eta\left(\frac{\partial p}{\partial v}\right)_\theta}{1 - \eta\left(\frac{\partial p}{\partial\theta}\right)_v}\Delta v = \left[\theta\left(\frac{\partial p}{\partial\theta}\right)_v - p\right]\Delta v.$$

The desired ratio of the internal work to the external work is given by

$$(35) \qquad \frac{\Delta W_1}{\Delta W_2} = \frac{\theta\left(\frac{\partial p}{\partial\theta}\right)_v - p}{p}.$$

This relation is true for all infinitesimal, reversible expansions in which the accompanying changes in p are infinitesimal. Values for $\Delta W_1/\Delta W_2$

for air have been computed and are to be found in the last columns of Tables II. and IV. The results have been platted in Fig. 4. In Fig. 4 only those points have been platted for which the corresponding computed values of μ and η were found to fall closely on the platted curves of Fig. 3. What has been noted previously regarding the uncertainties in $\theta(\partial p/\partial \theta)_v - p$ at low pressures, applies equally here. The changes in $\Delta W_1/\Delta W_2$ with pressure and with temperature are very evident, the ratio for the lower temperature and the higher pressures being greater than unity.

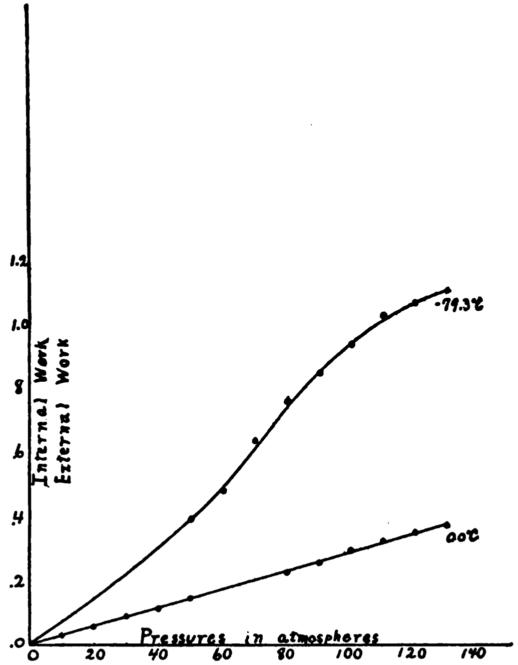


Fig. 4.

Variation with pressure of $\frac{\text{internal work}}{\text{external work}}$ in air for infinitesimal, reversible, isothermal expansions.

Results based on

Witkowski's data.................. ○

K. Onnes's equation.............. ●

Conclusions Regarding η, μ and $\Delta W_1/\Delta W_2$ of Air.— The plats show that in air for the region considered:

1. The free-expansion effect η is greater than the Joule-Kelvin effect μ for the same pressure and temperature.

2. The absolute difference between η and μ for the same pressure and temperature increases with increasing pressure.

3. Both η and μ are greater for the lower temperature than for the higher temperature.

4. Both η and μ beginning with low pressures, decrease with increasing pressures, the rate of decrease being the greater, the greater the pressure.

5. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\Delta W_1/\Delta W_2$ is greater at − 79.3° C. for a given pressure than at 0° C.

6. The ratio $\Delta W_1/\Delta W_2$ starts with zero values at zero pressure and increases with pressure, and in the case of the lower temperature, reaches a value greater than unity.

IV. THE DETERMINATION OF γ FOR CO_2 AS A FUNCTION OF THE PRESSURE AND THE TEMPERATURE.

Consideration of Existing Data.—There exist many determinations of γ for CO_2 under atmospheric pressure. There exist for pressures considerably greater, so far as the writer knows, only the computations of Amagat,[13] in which he combines the determinations of C_v made by Joly[22] with his own determinations of the interrelations of p, v and θ. His own work enabled him to determine $\theta(\partial p/\partial \theta)_v(\partial v/\partial \theta)_p$ for the gas at any desired pressure and temperature. By the application of (13), C_p and then γ were determined; first at varying pressures for a density of the CO_2 of .124 gr./cm.^{3}, then at varying pressures for a temperature of 50° C. He obtained various values for γ which showed that quantity to increase noticeably with increasing pressure and with decreasing temperature. For a temperature of 50° C. and a pressure of 100 atmospheres, he found γ to be 4.633. Unfortunately the results are such that it is impossible to check them by comparing them with other determined values at one atmosphere.

At about the same time there appeared papers by Lussana[23] on the values of C_p for CO_2 at about the same pressures and temperatures. Evidently his results might be combined with Amagat's, C_v determined and then γ; or his results might be combined with Joly's directly and γ thus determined. The writer has attempted the latter. It has been necessary to plat the given values of C_p and C_v in order to get values for C_p and C_v under the same conditions. Table VII. includes the results

TABLE VII.

γ for CO_2 from data by Joly and by Lussana.

p	30°			50°			80°		
	C_p	C_v	γ	C_p	C_v	γ	C_p	C_v	γ
10	.297	.169	1.76	.259	.169	1.53	.250	.168	1.49
20	.301	.173	1.75	.263	.172	1.53	.253	.171	1.48
30	.318	.179	1.72	.268	.177	1.52	.258	.175	1.48
40	.318	.184	1.73	.276	.182	1.52	.264	.180	1.47

p is expressed in atmospheres. C_p and C_v are expressed in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of such computations. Joly's conclusion, that for densities less than .124 gr./cm.^{3} C_v for CO_2 is practically independent of the temperature, was assumed as correct. There are only a few values which may be compared with those mentioned above as having been obtained by Amagat. There is but very little agreement between the two sets of determinations. Moreover the variations of γ in Table VII. are such as would indicate values of γ under atmospheric pressure which are very different from the generally accepted values. There is evident need of further determinations of γ for CO_2 for various pressures and temperatures.

Methods of Measuring γ for Gases under High Pressures.—There are several methods of determining γ which are practicable when applied to a gas under high pressures. There are (1) the thermodynamic method used by Witkowski as described briefly in an earlier part of the present paper; (2) the separate determination of C_p and C_v; (3) the determination of C_p and the consequent computation of C_v by equation (13); (4) the determination of C_v and the consequent determination of C_p by equation (13); (5) the method of Jamin and Richard[34] in which the isopiestic and isometric changes in temperature of a gas heated by a wire carrying an electric current is measured; (6) the method of Assmann,[35] in which there is observed the period of vibration of a system in a closed glass tube composed of a mass of the gas separated into two parts by means of a column of mercury; (7) the velocity of sound method; (8) the method of Lummer and Pringsheim[36] so modified as to apply to gases far removed from the state of perfect gas; and (9) the method of Maneuvrier,[37] a null method based on the same fundamental principles as the method commonly called after Clement and Desormes.

Reasons for Choosing the Method Selected.—The thermodynamic method of Witkowski might be applied to the data given by Amagat for CO_2. There would be required in addition however the variations of C_p or C_v with temperature at a given pressure such as atmospheric. Such determinations as these have been made but there is a great lack of consistency in the data. It has not seemed desirable to make use of this method in the present case. The next three methods necessitate the measurement of C_p, C_v or both for various pressures and temperatures. These are very difficult undertakings. Moreover, as they have already been measured by Joly and Lussana as noted above, and with very probable, serious errors as is suggested by Table VII., none of these three methods has been used in the present work. Jamin and Richard's method would undoubtedly be hard to realize under high pressure, especially in the carrying out of an isopiestic heating. Assmann's method might well yield good results, when all allowances are made for disturbing factors. The velocity of sound method has been used by Witkowski and by Koch for air with fair agreement of results with each other and with the former's results by the thermodynamic method. This method has been criticized by J. W. Capstick,[38] and by J. H. Jeans,[39] on account of a lag in the adjustment of the intermolecular and intramolecular energies of a gas on the passage of a sound wave through the gas. In Chapter XVI. of his "The Dynamical Theory of Gases" he concluded that any such lag in adjustment, provided that a certain supposition is true, "is in every way imperceptible." The method of Maneuvrier seemed free from this serious objection. It has been used. Practically, in Maneuvrier's method the compressions are no more reversible than those in sound experiments. Time, however, is given in this method for the practical balancing of the intramolecular and the intermolecular energies before actual measurements are made. The apparatus which was constructed for this work has been so designed as to make possible measurements according to a modification of Lummer and Pringsheim's method. However, time has not been found available for the perfection of this method, and consequently no measurements of that kind have been made.

Maneuvrier Method.—The method of Maneuvrier is based on a theorem due to Reech,[40] which is applicable to any substance whatever. A simple derivation of the equation expressing this theorem follows. Let *AB*, *AC*, *AD* and *DB*, Fig. 1, represent in this instance respectively infinitesimal reversible adiabatic, isothermal, isopiestic and isometric changes. Consider the change in internal energy which takes place when a substance is carried around the cycle *ADBA*. We have then

$$(C_p\Delta_1\theta - p\Delta v) + C_v(\Delta_2\theta - \Delta_1\theta) + p\Delta v = 0. \tag{36}$$

The two following relations are evident.

$$\Delta_2\theta = \left(\frac{\partial\theta}{\partial v}\right)_Q \Delta v. \tag{37}$$

$$\Delta_1\theta = \left(\frac{\partial\theta}{\partial v}\right)_p \Delta v. \tag{38}$$

There follows at once

$$\frac{C_p - C_v}{C_v}\left(\frac{\partial\theta}{\partial v}\right)_p = -\left(\frac{\partial\theta}{\partial v}\right)_Q, \tag{39}$$

or

$$\gamma = 1 - \left(\frac{\partial v}{\partial\theta}\right)_p \left(\frac{\partial\theta}{\partial v}\right)_Q. \tag{40}$$

By a process very similar to that involved in (8), (9) and (10), we get

$$\left(\frac{\partial\theta}{\partial v}\right)_Q = \left(\frac{\partial\theta}{\partial v}\right)_p + \left(\frac{\partial\theta}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_Q. \tag{41}$$

The application of (8) to an isopiestic process gives

$$\left(\frac{\partial v}{\partial\theta}\right)_p \left(\frac{\partial\theta}{\partial p}\right)_v = -\left(\frac{\partial v}{\partial p}\right)_\theta. \tag{42}$$

Equations (40), (41) and (42) give at once

$$\gamma = \left(\frac{\partial p}{\partial v}\right)_Q \left(\frac{\partial v}{\partial p}\right)_\theta, \tag{43}$$

which is the equation expressing Reech's theorem. In case (43) is applied to finite changes in which the changes in specific volume are small and equal, we have as a first approximation

$$\gamma = \frac{\Delta p_Q}{\Delta p_\theta}. \tag{44}$$

This is the form which has been used in the present work.

It was originally planned, and the apparatus was constructed with the aim in view of measuring both Δp_Q and Δp_θ directly with the apparatus. This general method was attempted, though no satisfactory results were obtained thereby. After repeated failures to get consistent values of γ, the plan was modified. According to this method Δp_Q was measured as planned; Δp_θ, however, was computed. The methods of obtaining Δp_Q and Δp_θ will be considered later.

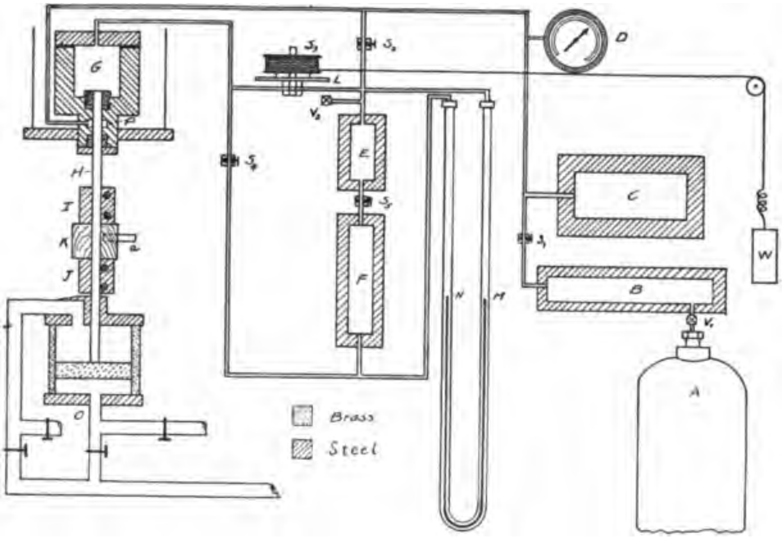
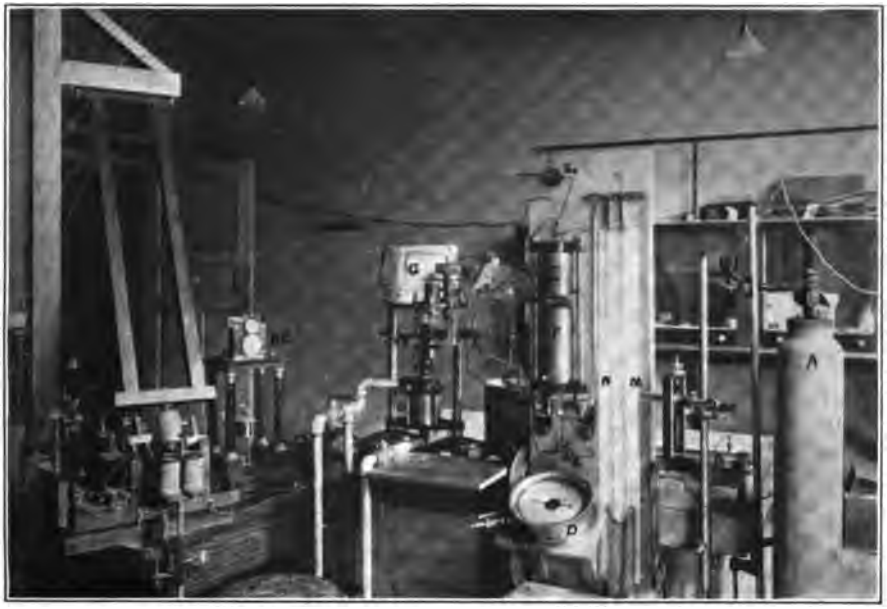


Fig. 5.

Apparatus.—The apparatus and the method of experimentation may be seen from an inspection of Fig. 5 (see also Plate I.) which represents the essential portions of the apparatus as finally connected and used. In general the arrangements and the materials have been so chosen as to withstand with safety pressures of 100 atmospheres though the actual highest pressure attained in these experiments was about 57 atmospheres. *A* represents the tube containing CO_2 under pressure which in the experiments to be considered was the source of the gas and of the pressure. *B* represents a cylinder of about 250 cm.^{3} capacity containing phosphorous pentoxide sprinkled through cotton-wool for the purpose of removing the moisture from the gas passing through it. *C* represents a distributing chamber of about 600 cm.^{3} capacity which also served as a maintainer of the pressure in the protective system to be spoken of later. At the stop-cock S_2, the gas enters the system where it is to be experimented with. *D* is a Bourdon steam test-gauge reading to 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ by steps of 5 $\frac{\text{lbs. wt.}}{\text{in.}^2}$. *E* and *F* are chambers of respectively 150 cm.^{3} and 300 cm.^{3} capacity connected with the arms *M* and *N* of the differential, mercurial manometer. This manometer also served as a manoscope. The combination is the same as that used by Maneuvrier in his original work. The purposes of *E* and *F* are merely to give large volumes to the gas chambers of the manometer so that, in case a small leak should occur in either of these gas chambers, the rate of change of pressure in it should be negligible. *E* and *F* are separated by a stop-cock S_5 which in the final arrangement was not used. *G* is the compression chamber which contains the gas to be compressed or rarified. It has a capacity of about 300 cm.^{3} and is surrounded by a bath which contains a thermoregulator and a stirer (not shown in Fig. 5 nor in Plate I.). The volume of *G* can be increased or diminished at will by means of the device indicated at *O* which is actuated by compressed air. Chambers *B*, *C*, *E*, *F* and *G* are all japanned on the inner surfaces for the purpose of preservation and chamber *G* for the added purpose of surrounding the contained gas with a poor conductor for heat. *H* is a piston rod to which are clamped two stops *I* and *J* which are separated by a block of hard oak wood *K*. The use of different blocks of wood for *K* permits of different changes of volume in chamber *G* due to the thrusting in of the piston rod *H*. The lower stop *J* is firmly fixed to the rod *H* in order that, when *H* is in its lowest position, the volume of *G* is certain to be very closely a fixed amount. V_1 and V_2 are pin valves. S_1, S_2, S_3, S_4 and S_5 are stop-cocks. As already noted, S_5 was not made use of in the apparatus as finally arranged. The construction of S_3 is shown in Fig. 6. S_1, S_2, S_4 and S_5 differ from S_3 only in having the special device attached to the pin of S_3 replaced by a bar so that the pin may be rotated by hand. The pin of S_3 is rotated by a heavy weight *W* attached to a heavy spring which in turn is attached to a slender rope made of several strands of heavy fish-line, one end of which is wound about the wooden drum fastened to the pin of S_3. The pin of S_3 is provided with an arm *L* which serves



A. G. WORTHING.

PLATE I.

as a catch. The spring removes the sudden jolt that otherwise would be experienced on the sudden stoppage of the rotation of the pin of S_3. The final ground surfaces of the pin and stock were produced by grinding them in powdered quartz and, sometimes, in pumice. In Fig. 5 a small tube is shown connecting *C* with *P*. The pressure in *C* was always nearly equal to that in the system *EFGMN*. Consequently this connection at *P* together with the packing about *H* permits at the most, of only a slow leakage of gas into or out of *G* through the packing and along the surface of *H*. Similar tubes lead from *C* to all the stop-cocks. They are connected to the stop-cocks at points which lead directly to the grooves *Q* (Fig. 6). These grooves entirely surround the pin of the stop-cock. As before the pressure in *C* is distributed through the tube to *Q* where it prevents the leakage of gas from or into the system *EFGMN*. The small tubing connecting the various chambers and stop-cocks is of copper. The external and internal diameters are respectively .32 cm. and .16 cm. The method of making the unions of these tubes with the other portions of the apparatus is well illustrated in Fig. 6. The external and internal diameters of the glass tubing used in the manometer are respectively .80 cm. and .30 cm. The stop-cocks are of brass, the chambers *B*, *C*, *E*, *F* and *G* were cut out of steel shafting.

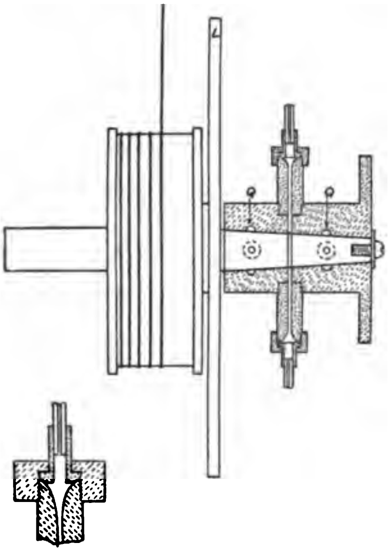


Fig. 6.

In the method of experimentation pursued it was necessary to vary and to measure the time interval between the compression of the gas in *G* (Fig. 5) and the opening of the S_3. This was brought about by means of the apparatus diagrammed in Fig. 7. The block of oak wood, *K* (Fig. 5) carries a projecting metal prong *a*. The thrusting in or out of *H* brings *a* in contact with *b* and *c*. The contact *ab* closes an electrical circuit through the electro-magnet *d*, the energizing of which releases a pendulum which in its motion closes at *e* an electrical circuit through the electro-magnet *f*, opens at *g* the same circuit, and breaks at *h* by a device not indicated, the circuit containing the electro-magnet *d*. The current through the circuit closed at *e* actuates the electromagnet *f*, thus releasing the catch *L* attached to the pin of stop-cock S_3. The weight *W* causes the rotation of the pin of S_3. The breaking of the circuit at *g* is followed by the demagnetizing of *f*, and the catch *L*, after a rotation of the pin of 180°, is caught and the rotation of the pin is suddenly stopped. In case there is contact at *e* when the plunger *H* is moved in, the electromagnets in the circuits at *d* and *f* are actuated simultaneously. Thus by having the circuit at *e* initially closed or broken two different time intervals may be had between the compression of the gas in *G* and the opening of the cock S_3. Other intervals may be had by varying *W* and the position of *e* on the pendulum apparatus. The contact *ac* permits a current to flow through the commutation device on the drum *i* of S_3 through the electro-magnet of a Hipp's chronoscope (H.C.). At *j* this current is broken when the stop-cock S_3 is open, as may be seen by inspecting the diagram of the commutating device. S_3 is diagrammed in a closed position. Thus the chronoscope records the time elasping between the plunging in or out of *H* (Fig. 5) and the opening of the stop-cock S_3. Previous to July 28th, however, a slightly different method was used. The interval measured was from the plunging in or out of *H* to the closing of S_3.

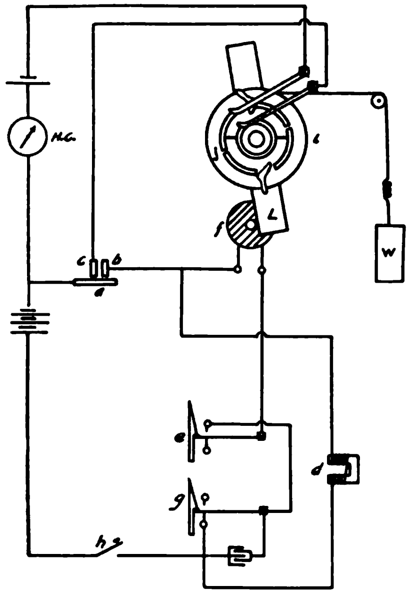


Fig. 7.

Stop-cock Difficulties.—Originally it was planned to use tallow as the stop-cock lubricant, and to have the openings to *Q* and the grooves *Q* of the stop-cocks (Fig. 6) filled with gas directly connected with that in *C*. It was soon very evident that this plan must be abandoned. With this arrangement, pressures of a few atmospheres could be maintained for an hour at most. A great deal of time was spent in the search for some stop-cock fluid which should be able to withstand the high pressures. The fluid finally used was formed by dissolving approximately one part of rubber in three parts of hot pine-tar. The solution was heated and the more volatile gases driven off until the desired consistency was reached. This fluid when cool is very viscous and sticky. It was introduced in the openings leading to Q and in the grooves Q. It did quite well and often for several hours, no noticeable leaks in the apparatus could be detected. With the very highest pressures the fluid was gradually forced out between the pin and the stock of the stop-cocks. However, there was no leakage of gas to the outside, until a complete passage-way to the outside for the gas back of the rubber-tar solution had been formed. As soon as such a passage-way was formed, the desired gas pressure in C was usually very hard to maintain by the admission of gas through S_1 and it was necessary to discontinue the experiment, empty the apparatus and refill the receptacles with the rubber-tar solution. For further work with this apparatus, considerably enlarged receptacles for the stop-cock fluid should be provided.

The Experimental Determination of Δp_Q.—In the filling of the apparatus with the gas to be experimented upon, it was necessary to be sure that the gas was dry and that whatever air was in the apparatus initially was removed or nearly so. The moisture was removed by the phosphorus pentoxide in B (Fig. 5). The phosphorus pentoxide was replaced by a fresh supply several times. In each instance, that furthest from the entrance to chamber B was found when removed to be a dry powder, thus indicating that in all cases the carbon dioxide gas experimented on was free from moisture. The removal of the air was accomplished partially with a hand pump, then carbon dioxide was allowed to fill the exhausted space. This mixture of air and carbon dioxide was then pumped out and the process repeated until it was certain that not more than .05 per cent. of the gas in the apparatus was of the original air. After the desired pressure throughout the apparatus including the protective system had been reached and had become steady due to the temperature having reached a steady state, S_3 was closed. Then, depending on whether the change in the compression chamber G was to be a compression or a rarefaction, the pressure in the protective system and in E and M was increased or decreased until the expected change in pressure in the compression chamber was equal to the difference indicated by the mercury levels in M and N. Then S_4 was closed. At this stage, it is to be kept in mind, the pressure in the compression chamber G was the same as that in F and that at the upper surface of the mercury in N; and that the pressure in E was the same as that in M. Now with the rapid successive opening and closing of the valves letting compressed air into and out from O, the gas in G was compressed or rarified due to the motion of the piston H, contact was made at *ab* and *ac* (Fig. 7), as explained above; the pin of S_3 was rotated connecting for a short space of time chambers E and G; and the time interval between the making of the contact *ac* and the opening of S_3 was recorded by the Hipp's chronoscope H.C. This was very quickly followed by the reverse movement of the piston H in order that there might be but a very small amount of heat lost or gained by the gas in the compression chamber as a result of the heating or cooling from the previous direct motion of H. In case the pressures in G and M were not equal on the opening of S_3, a passage of gas must necessarily have taken place through S_3; and, on the return of H to its initial position, S_4 was opened. There was a readjustment of pressure then in G, F, and N and also in E and M. When a steady state was reached, usually after a minute or so, the process beginning with the closing of S_4 was repeated. In fact it was necessary to repeat again and again until, by the automatic transference of gas through S_3 from G into E or vice versa, there should occur for at least for two successive repetitions no transference of gas from E to G or vice versa. This condition was determined by an observer looking through a cathetometer telescope at the upper mercury surface in M or in N. Whenever in the process described above there occurred a transfer of gas from G to E or vice versa, there was a shift in the mercury level. When a condition of balance obtained, no further shifting of the mercury surface could be noted, in fact no distortion of the surface could be detected. With the apparatus in working order, it usually did not require more than ten trials before the balance was obtained. The actual difference of pressure produced in the compression chamber and existing after the time interval shown by the Hipp's chronoscope, was measured on the differential manometer MN by means of the cathetometer. By varying the initial conditions at the contact *e* (Fig. 7), data corresponding to two time intervals may be obtained.

Now, if it may be assumed here that the change in *the change in pressure* due to heat being conducted to or from the gas in G is a linear function of the time for short intervals of time, we may obtain the change in pressure which would have occurred in G if the time interval had been infinitesimal. Let Δp_1 and Δp_2 be changes in pressure and Δt_1 and Δt_2 be the corresponding intervals of time in the above described experiment. Let Δp_0 be the change in pressure for an infinitesimal interval. Then we have

$$\Delta p_0 = \Delta p_1 - \frac{\Delta p_2 - \Delta p_1}{\Delta t_2 - \Delta t_1} \Delta t_1 . \tag{45}$$

Δp_0 is the Δp_Q of (44). Data from certain preliminary measurements obtained July 25 and platted in Fig. 8, indicate that the assumption is not far from true. Near the completion of the experimental work, other attempts were made to test (45) more carefully. In each instance, certain accidental changes occurred which made impossible the obtaining of the desired number of different intervals under conditions which would be necessary for a rigid test. Even if the assumption made is not true, the actual variation from it could hardly be such as to cause any serious error.

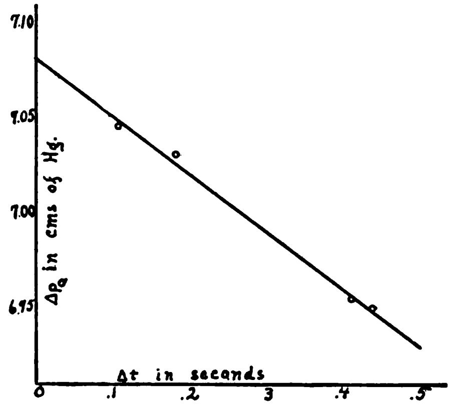


Fig. 8.

Experimental test of assumption made in (45)

It is perhaps well to note here certain precautions taken to insure accuracy. The pressure gauge was always adjusted so that the index was aligned with some desired division on the dial. The face of the gauge was always tapped lightly to insure the freedom of movement of the indicating parts. Parallax was carefully eliminated. A single division on the dial corresponded to $5\,\frac{\text{lbs. wt.}}{\text{in.}^2}$. A variation of one twentieth of a division was noticeable. This corresponds to about one sixtieth of an atmosphere. Actual trials showed that any desired pressure could be certainly obtained (assuming the gauge to be correct) to within 1.5 cm. of Hg. To prevent any errors due to the sticking of the mercury in the manometer tube, the glass tubes *M* and *N* were tapped just before and just after the compression or rarefaction in *G* was produced. To further eliminate such troubles, the initial pressure in *E* for one determination of Δp_Q for a given p and T was first made too great and for the next determination under the same conditions was made too small, in order that in the self-adjusting process there would in the first case be a slight movement of the mercury in *N* upwards and then in the second case downwards. The two values of Δp_Q obtained thus were always in very good agreement, they always differed in such a manner as to indicate that there was some sticking of the mercury to the manometer tubes. These differences in Δp_Q, with a few exceptions relating to measurements especially difficult, did not amount to more than .6 mm. of Hg and usually were much less. The average of two such values for Δp_Q were taken as the observed value. When it is considered that the actual values of Δp_Q varied from 5 to 13 cm. of Hg, it will be seen that the uncertainties arising from this source will generally be quite small. In order to eliminate any errors in the measurement of Δp_Q due to leakage of gas during the measurements of the heights of the mercury columns in M and N, one observer noted during this process with the aid of a traveling microscope the slow motion, if it existed, of the mercury in column M. Corrections to the cathetometer readings for such leakages were readily made. In addition to the ordinary precautions for cathetometer work, double settings were made. If the readings from these double settings were not consistent with the difference noted on the traveling micrometer, further readings were taken.

In order that a clear idea of the method of procedure may be obtained, certain of the records for the afternoon of August 12 are presented in Table VIII., together with certain explanatory notes. C and R indicate

TABLE VIII.

Sample note book records showing experimental details for determination of Δp_Q.
Aug. 12, 1910, P. M.

Movement of compressing piston with blocks no. 3 and no. 4 at K (Fig. 4).

Mean of five determinations at the beginning	1.435 cm.
Mean of five determinations at the end	1.426 "
Av.	1.430 "

Gauge reading: $300 \frac{\text{lbs. wt.}}{\text{in.}^2}$.

Collected data:

Room Temp.	Bath Temp.	Change.	N in cm.	M in cm.	$M-N$ in cm.	Adjustment.	Interval in Sec.	Remarks.
26.6°	50.0°	C.	92.672	83.395	9.277	down	.095	?
.6	"	"	.658	.412	.246	up	.098	good
.6	"	"	.627	.430	.197	down	.070	good
.5	"	"	.610	.470	.140	down	.314	
.4	"	"	.630	.435	.195	up	.310	
.4	"	R	82.321	92.552	.231	up	.090	
.2	"	"	.340	.540	.200	down	.090	
.2	"	"	.365	.516	.151	up	.304	
.1	"	"	.390	.515	.125	down	.304	

Note book records from which N, M and interval entries of the fourth observation were taken.

N' in cm.	Chronoscope Reading.	Chronoscope Interval.	N'' in cm.	N in cm.	M in cm.	Traveling Microscope Reading in cm.
	005			92.610		8.911
32.61	163	158	32.60	.605		15
.60	322	159	.59		83.480	19
.59	475	153	.59		.480	21
.59	632	157	.59	Corrected 92.610	83.470	

respectively a compression and a rarefaction. The N and M readings are the cathetometer readings on the mercury meniscuses in tubes N and M (Fig. 5). $M \sim N$ represents the numerical difference between M and N. The adjustments "up" and "down" indicate that, in the self-adjustment of the gas pressure preceding the equilibrium, the motions of the mercury surface in N during a compression and in M during a rarefaction were "up" and "down" respectively. The "interval" measured is the time elapsing between the making of the circuit at ac (Fig. 7) and the breaking of the circuit at j. It is thus the interval between the plunging in of the piston H and the opening of stop-cock S_2 so that chambers E and G were in communication. Under remarks it is noted that the first observation was considered questionable when taken. It does not check up with the other observations from the standpoint of the variation in Δp_Q due to up and down adjustments. It has been discarded in the further computational work. The readings N' were read on a rough paper scale back of tube N with the aid of the cathetometer telescope, just before the gas in G was compressed; the readings N'' were taken in a similar manner just after. The unit of the chronoscope readings was .002 sec. The average interval was therefore .314 sec. The slight variations in the individual intervals are partially to be accounted for by the fact that the weight W (Fig. 5) was usually still being vibrated up and down somewhat by the spring above it when a new compression was about to be made. The method of obtaining the corrected N and M readings is evident. From the collected observations given, there are to be obtained as indicated above with the aid of (45) and on correcting $M \sim N$ to 0° C., data recorded in the first six columns of Table XIII. under the proper date. Nearly all such data relating to Δp_Q represent values obtained in the manner indicated above, with the exception that usually only two observations, one an "up," the other a "down" for the same interval were taken either for the rarefaction or for the compression. In computing Δp_Q by (45), the term multiplying Δt, was assumed to be the same as in the other process for which the regular four observations were taken.

The Computations for Δp_θ.—Kamerlingh Onnes[41] has given an empirical equation of state for CO_2 which is founded on Amagat's work and which represents Amagat's data with a very high degree of accuracy. The equation is of the form

$$\lambda \pi \nu = A + \frac{B}{\lambda \nu} + \frac{C}{(\lambda \nu)^2} + \frac{D}{(\lambda \nu)^4} + \frac{E}{(\lambda \nu)^6} + \frac{F}{(\lambda \nu)^8}, \tag{46}$$

where

$$\lambda = \frac{p_c v_c}{\theta_c}, \quad p_c = \frac{p}{\pi}, \quad \theta_c = \frac{\theta}{\tau} \text{ and } v_c = \frac{v}{\nu}, \tag{47}$$

v being expressed in $\frac{\text{T. N. V. Units}}{\text{gr. x mol.}}$; and where A, B, C, etc., are functions of θ such that

$$(48)\qquad \begin{aligned} A &= a_1\tau, \\ B &= b_1\tau + b_2 + b_3/\tau + b_4/\tau^3, \\ C &= c_1\tau + c_2 + c_3/\tau + c_4/\tau^3, \\ &\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \\ F &= f_1\tau + f_2 + f_3/\tau + f_4/\tau^3. \end{aligned}$$

(46) was used in this work. It was found that in no case were there appreciable errors introduced in the present work by neglecting the terms containing D, E and F. Table IX. gives the necessary constants.

TABLE IX.

Constants for (47).

Subscript.	1	2	3	4
10^4a	36.62			
10^8b	173.6	−321.3	−.241.5	−82.4
$10^{11}c$	66.2	− 47.6	111.2	103.6

In the computations connected with the present work the values of v were expressed for the most part in $\frac{\text{N. V. units}}{\text{gr. mol.}}$ in order to check the computations based on K. Onnes's equation with the experimental data of Amagat.[29] In determining Δp_θ the following expansion was used

$$(49)\qquad \Delta p_\theta = \left(\frac{\partial p}{\partial v}\right)_\theta \Delta v\left[1 + \frac{1}{2}\frac{\left(\frac{\partial^2 p}{\partial v^2}\right)_\theta}{\left(\frac{\partial p}{\partial v}\right)_\theta}\Delta v + \frac{1}{6}\frac{\left(\frac{\partial^3 p}{\partial v^3}\right)_\theta}{\left(\frac{\partial p}{\partial v}\right)_\theta}(\Delta v)^2\right].$$

Substitutions in (49) by means of (46), (47) and (48) give, neglecting terms with $\Delta v/v$ to the fourth and higher powers,

$$(50)\qquad \Delta p_\theta = \left(\frac{\partial p}{\partial v}\right)_\theta \frac{\Delta v}{v}\left[1 - \beta\frac{\Delta v}{v} + \left(\frac{\Delta v}{v}\right)^2\right]v,$$

where

$$(51)\qquad \beta = 1 + \frac{B}{A}\frac{\theta_c}{p_c}\frac{\alpha}{v} + \frac{3AC - 2B^2}{A^2}\frac{\theta_c^2}{p_c^2}\frac{\alpha^2}{v^2},$$

in which α is the ratio of the two specific volume units, 1.00706. The term of (50) containing β is of the second order, consequently it is sufficient to have β approximately. Table X. gives such values to the nearest

TABLE X.

Values of β for equation (50).

p in Atmos.	7.78	14.72	21.52	28.52	35.52	42.34	49.36	57.0
0° C.	.94	.88	.78	.66				
30	.96	.92	.87	.81	.74	.66	.55	.39
50	.97	.94	.90	.86	.82	.77	.71	.63
100	.98	.96	.95	.93	.91	.89	.87	.84

hundredth. Column 7, Table XI. contains the results of such computations for Δp_θ.

Calibrations and Miscellaneous Notes.—It should be noted here that various parts of the apparatus were carefully calibrated and measured. The differential surface tension effects in the manometer were always negligible. The changes in the density of the mercury due to the varying pressure were also found negligible. It was always to be noted on releasing the pressure in the apparatus that some CO_2 had been dissolved in the mercury. The amount was small, and, considering the limited amount of time at the writers' disposal, it never seemed sufficient to warrant an investigation. The possible effect of the dissolved CO_2 on the density of the mercury has been ignored. The pressure gauge was a Bowden steam test gauge of 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ range. It was carefully calibrated. In determining the pressure of the gas in the apparatus account was taken of the barometric pressure. Throughout the time of experimentation this was .97 atmo. The thermometers were compared with standard thermometers. The volume of the compression chamber was obtained by finding the weight of the water necessary to fill it. The

TABLE XI.

Data for and results on γ for CO_2. Preliminary Results.

Date.	Temp. of Bath.	p in Atmos.	Change.	Piston Motion in cm.	Δp_Q in cm. of *Hg*.	Δp_θ in cm. of *Hg*.	γ	γ (corr.)	γ'	Purity of CO_2 in %.
July 22	29.4	14.72	C	3.004	13.10	9.77	1.342	1.340		99.2
25	32.7	7.78	C	3.004	7.04	5.37	1.310	1.311		99.6
27	32.4	14.72	C	3.004	13.24	9.79	1.352	1.350		
30	32.2	28.52	C	1.422	12.09	8.04	1.503	1.508		
Aug. 1	31.0	7.78	C	1.422	3.348	2.529	1.324	1.325		
3	31.4	7.78	C	1.422	3.337	2.528	1.320	1.320		
4	31.8	7.78	R	1.422	3.326	2.507	1.326	1.327		
5	31.7	7.78	C	2.122	4.94	3.48	1.306	1.306		
5	31.4	7.78	C	2.122	4.97	3.78	1.314	1.315		

Table XI.—*Continued.*

Data for and results on γ for CO_2. *Final Results.*

Date.	Temp. of Bath.	p in Atmos.	Change.	Piston Motion in cm.	Δp_Q in cm. of *Hg*.	Δp_θ in cm. of *Hg*.	γ	γ (corr.)	γ'	Purity of CO_2 in %.
8	31.3	7.78	C	3.004	7.09	5.37	1.320	1.320	1.268	
9	30.8	7.78	R	3.004	7.01	5.32	1.317	1.317	69	
	31.5	14.72	R	3.004	13.20	9.71	1.359	1.360	63	
	32.2	14.72	R	1.422	6.18	4.60	1.344	1.346	50	
	31.7	14.72	C	1.422	6.23	4.61	1.352	1.353	51	99.6
10	31.2	28.52	C	1.428	12.05	8.09	1.488	1.489	50	
	31.8	28.52	R	1.428	12.14	8.06	1.505	1.509	63	
11	31.3	21.52	R	1.407	9.06	6.32	1.432	1.433	63	99.6
	31.2	21.52	C	1.407	9.09	6.34	1.434	1.434	62	
12	49.8	7.78	C	2.994	6.99	5.39	1.296	1.296	54	
	49.9	7.78	R	2.994	7.04	5.34	1.316	1.316	51	
	49.9	14.72	R	2.994	13.11	9.91	1.335	1.335	60	
	49.9	14.72	C	2.994	13.29	9.89	1.345	1.345	62	
	50.0	21.52	C	1.430	9.19	6.63	1.386	1.386	57	
	50.0	21.52	R	1.430	9.20	6.61	1.391	1.391	65	
13	50.0	28.52	C	1.421	12.15	8.39	1.448	1.448	61	
	50.1	28.52	R	1.421	12.10	8.37	1.447	1.447	64	
	50.2	34.52	R	.768	8.20	5.38	1.524	1.525	69	
	50.2	34.52	C	.768	8.16	5.39	1.515	1.516	62	
15	98.4	7.78	C	3.020	6.93	5.52	1.256	1.256	35	
	98.4	7.78	R	3.020	6.91	5.47	1.264	1.264	47	
	98.5	14.72	C	1.436	6.17	4.86	1.269	1.269	27	
	98.4	14.72	R	1.436	6.17	4.84	1.275	1.275	34	99.5
16	98.5	28.52	C	1.438	12.06	9.07	1.329	1.329	36	
	98.5	28.52	R	1.438	11.99	9.04	1.326	1.326	36	
	98.6	41.34	R	1.775	9.83	6.96	1.412	1.413	66	
	98.6	41.34	C	1.775	9.77	6.97	1.401	1.402	55	99.3
17	0.2	28.52	C	.786	6.49	3.83	1.694	1.694	48	
	0.2	28.52	C	1.425	11.91	6.95	1.710	1.710	34	
	0.2	28.52	R	1.425	11.81	6.94	1.702	1.702	32	
18	0.2	21.52	C	1.424	8.97	5.07	1.528	1.528	32	
	30.9	41.34	C	.786	9.93	5.61	1.771	1.770	59	
22	0.2	7.78	C	2.120	4.95	3.70	1.338	1.338	58	
	0.2	7.78	R	2.120	4.95	3.67	1.346	1.346	68	
23	98.6	34.52	C	.805	8.24	6.19	1.331	1.332	14	
	98.6	34.52	R	.805	8.27	6.18	1.339	1.340	24	
	98.6	48.36	C	.809	11.78	8.28	1.423	1.425	50	
24	31.6	7.78	C	4.388	10.31	7.88	1.309	1.309	57	
25	30.7	57.0	C	.798	13.78	5.85	2.36	2.35	82	
	31.1	7.78	C	3.038	7.12	5.43	1.310	1.310	58	

γ (corr.) indicates values of γ corrected to the standard temperatures 0°, 31°, 50° and 98.5° C.

volume of the chamber and its accessories is 310.0 cm^3. The average of 20 measurements of the diameter of the compressing piston gave 1.1098 cm. The purity of the gas was determined by bringing a known quantity of it into contact with KOH.

The time required for the thrusting in of the plunger H (Fig. 5) is a matter of some interest. If the thrusting in of the plunger and the reaching of a steady state by the gas could possibly occur in an extremely short interval such as .001 sec., one would need to give special consideration to the extremely high temperature gradient which would be established at the boundaries of the vessel. If, however, each of the two processes should take an appreciable time, no very high temperature gradient is to be expected at any instant. The time of inthrust of the plunger H was determined by taking the difference between two selected intervals. The first interval was from the starting of the plunger H to the opening of stop-cock S_2, the interval being recorded in the manner described above by the chronoscope. The second interval differed from the first in that the contact beginning the interval was made near the end of the inthrust instead of at the beginning. The average of several such determinations showed that the time for the maximum inthrust was about .06 sec. In the measurements made this interval of inthrust was always included. Of course, for the smaller inthrusts, this interval was smaller.

Data and Results.—The data taken and the values of γ obtained are shown in Table XI. The values given may in a few cases differ by .001 from the quotient of Δp_Q by Δp_θ because of the manner in which the former were obtained. The corrections for obtaining γ (corr.) for the four standard temperatures were obtained from an initial rough plat. The computed values of γ for these four standard temperatures have been platted in Fig. 9 as a function of the pressure. With a few exceptions, each platted point represents the mean of two determinations of γ, one from a compression, the other from a rarefaction. Two pairs of such values have been included in the point for the gas at 31° C. and a pressure of 7.78 atmospheres. The higher values were obtained early in the work. The lower values were obtained near the end. Sometime between August 18 and August 23, the date unfortunately not being recorded, the rubber washer between the compression chamber and its lid was replaced by a new one, which was noticeably thicker than the one removed. The importance of the consequent change in the volume of the compression chamber was not appreciated fully at the time or accurate measurements would have been taken. Account has not been taken of this change in the computations. However, if account should be taken of this change of volume, the separately determined values would more nearly coincide. The same is to be said regarding the values for γ at 98.5° C. for pressures of 35.52 atmospheres and 49.36 atmospheres. In this instance the values of γ taking account of the volume change would also be raised so that the variations of the platted γ for this temperature would be less noticeable. The same possibility applies to γ for 0.2° C. at 7.78 atmospheres. It is to be noted that the preliminary values of γ, though not platted, agree very well with the final results.

Result of Maneuvrier and Results Based on C_v by Joly.—There is platted for comparison purposes the value of 1.298 determined by Maneuvrier,[27] the originator of this method, for CO_2 at atmospheric pressure and 10° C. Values of γ for CO_2 at atmospheric pressure have been rather discordant. Generally, however, such values approximate the results obtained here, though the variation with temperature has been found to be less noticeable than what the writer has obtained. There are also platted values of γ which are based on determinations of C_v by Joly. The method of computing was that used by Amagat.[31] Values of C_v and p, v, θ relations from the experimental data of Amagat were combined according to (13). This has been done by Amagat. The writer has not been able to verify fully the computations of Amagat and has here incorporated results from his own computations. The writer in determining $(\partial p/\partial \theta)_v$ and $(\partial v/\partial \theta)_p$

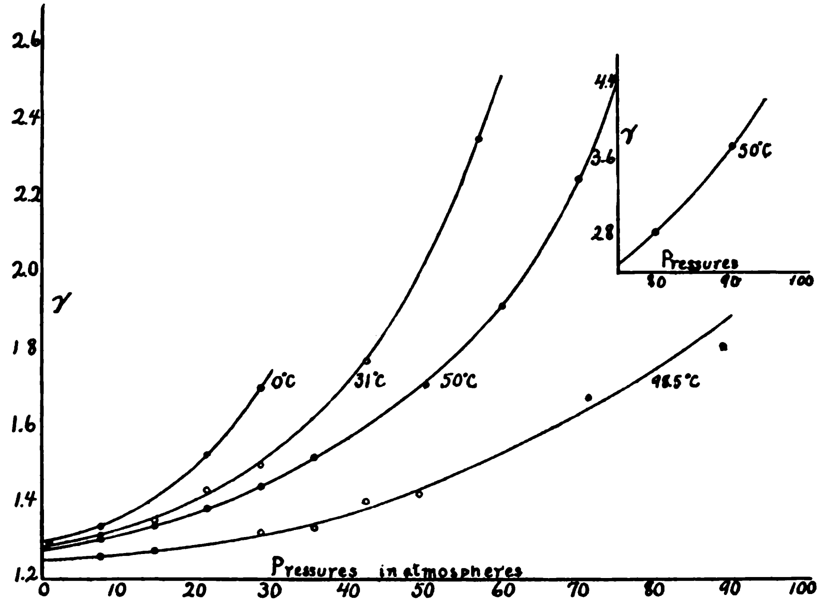


Fig. 9.

Variation of γ in CO_2 with pressure and temperature.

Results based on determinations

of C_v by Joly	●
of Δp_a by Worthing	○
of Maneuvrier	+

has used a graphical method. The values determined represent true values for the temperatures and pressures indicated. The values of C_v for pressures of 80 and 90 atmospheres at 50° C. have been taken from Amagat's extrapolation. The values for C_v at 100° C. result directly from equations given by Joly for CO_2 at densities .1240 gr./cm.^{3} and .1800 gr./cm.^{3} Table XII. includes these data and results. The general agreement is quite satisfying.

Table XII.

Data for and results on γ for CO_2 based on C_v determinations by Joly and p, v, θ determinations by Amagat.

7	p	C_v	$C_v\left(\frac{\partial v}{\partial \theta}\right)_p$	$-\left(\frac{\partial p}{\partial v}\right)_\theta$	C_p	γ
50°C.	50	.1920	$.0_3 1310$	2020	.329	1.710
	60	.2015	1280	2850	.386	1.915
	70	.2108	1345	3670	.474	2.245
	80	.2303	1530	4560	.644	2.83
	90	.2585	1800	5500	.945	3.73
100	71.3	.1902	0870	3690	.318	1.670
	87.8	.2056	0805	5590	.372	1.810

p is expressed in atmospheres, C_p and C_v in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$.

γ' of Equation $pv^{\gamma'}$ = constant.—In the column (Table XI.) headed γ' are included values which are derived on the assumption that for the processes of compression and rarefaction considered, there holds the following relation:

$$pv^{\gamma'} = \text{constant}. \tag{52}$$

The approximate constancy of γ' for a given temperature is remarkable and is worthy of further experimental consideration. A γ', of course, is not to be interpreted as a ratio of the two heat capacities except perhaps for the gas under zero pressure at the same temperature, or as described by the same adiabat, or under some other similar conditions. Differentiation of (52) and the application of (43) give

$$\left(\frac{\partial p}{\partial v}\right)_Q = -\gamma'\frac{p}{v} = \gamma\left(\frac{\partial p}{\partial v}\right)_\theta. \tag{53}$$

Whence

$$\gamma = -\gamma'\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_\theta, \tag{54}$$

or according to Bakker[30]

$$\frac{\gamma - \gamma'}{\gamma'} = -\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_\theta - 1 = \text{departure of gas from Boyle's law.} \tag{55}$$

Extrapolation to zero presssure, making use of these values of γ', would seem to indicate that the platted curves of γ (Fig. 9), on being extrapolated back to zero pressure, had been extrapolated to too high values of γ. Not a great deal of dependence may be placed on this, however, until more is known about the function γ'.

Conclusions regarding γ and γ'.—The plats and tables show for CO_2 for the region considered:

1. The ratio of the two heat capacities γ for a given pressure decreases with an increase of temperature.

2. γ for a given temperature increases with pressure.

3. The curve for γ at 30° C. is such as to be consistent with the theoretical infinite value of γ at the critical point.

4. The agreement of the values based on Δp_Q data with those based on C_v data by Joly is very good.

5. The results at atmospheric pressure are in fair agreement with the results of others.

6. γ', where $pv^{\gamma'}$ = constant applies to reversible adiabatic changes, is approximately constant.

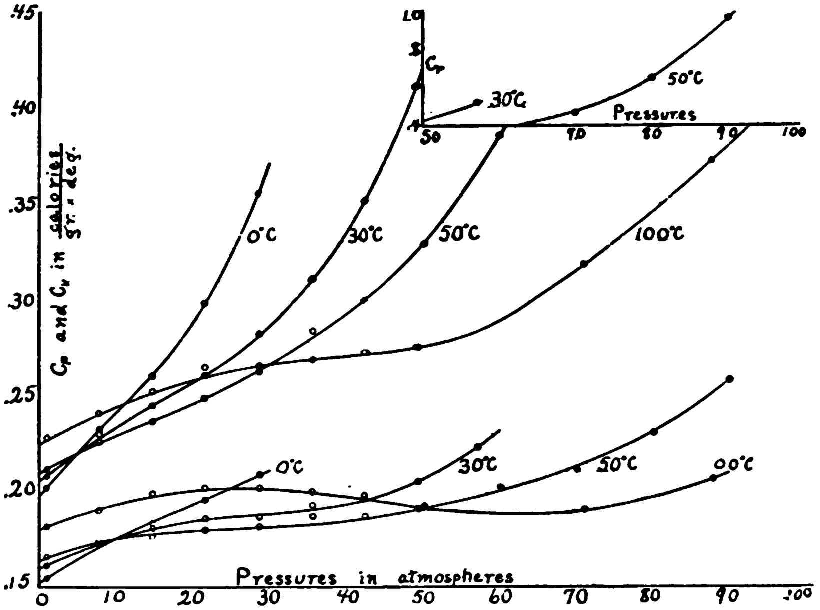


Fig. 10.

Variation of C_p and C_v of CO_2 with pressure and temperature.
Results based on determinations
of C_v by Joly.. ●
of γ by Worthing.. o

V. DETERMINATION OF C_v AND C_p FOR CO_2.

Determinations from the Present Work.—Equation (13) gives at once

$$(\gamma - 1)C_v = \theta \left(\frac{\partial p}{\partial \theta}\right)_v \left(\frac{\partial v}{\partial \theta}\right)_p . \tag{56}$$

This enables one to determine C_v and hence C_p by means of the data already obtained. The method of computation is evident. The transformation factor used in this work in the changing of the units of C_v and C_p to the ordinary units is expressed in (57).

$$1 \frac{\text{atmos.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}} = 12.24 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}} . \tag{57}$$

Values of C_v and C_p are to be found in Table XIII. Values of $(\partial p/\partial \theta)_v$, $(\partial v/\partial \theta)_p$ and $\theta(\partial p/\partial \theta)_v(\partial v/\partial \theta)_p$ are included in the hope that they may save some one otherwise extended computations. In Fig. 10 C_v and

TABLE XIII.

Data for and results on C_p and C_v of CO_2.

T	p	γ	$\log\left(\frac{\partial p}{\partial \theta}\right)_v$	$\log\left(\frac{\partial v}{\partial \theta}\right)_p$	$\log\left[\theta\left(\frac{\partial p}{\partial \theta}\right)_v\left(\frac{\partial v}{\partial \theta}\right)_p\right]$	C_v	C_p
0	7.78	1.342	$\bar{2}.5130$	$\bar{4}.7359$	$\bar{3}.6852$	.173	.233
	14.72	1.418	.8459	.5156	.8856	.184	.261
	21.52	1.528	$\bar{1}.0707$	.4206	.9276	.196	.299
	28.52	1.702	.2630	.3796	$\bar{2}.0789$	.209	.356
30	7.78	1.314	$\bar{2}.4501$	.7169	$\bar{3}.6486$	.174	.230
	14.72	1.360	.7652	.4770	.7238	.180	.245
	21.52	1.420	.9680	.3545	.8041	.186	.265
	28.52	1.509	$\bar{1}.1315$	.2778	.8909	.187	.282
	35.52	1.621	.2727	.2362	.9905	.193	.311
	42.34	1.779	.3978	.2203	$\bar{2}.0997$	.198	.353
	49.36	2.01	.5200	.2271	.2287	.205	.412
	57.0	2.37	.6540	.2602	.3958	.223	.528
50	7.78	1.304	$\bar{2}.4143$	.7092	$\bar{3}.6328$	.173	.226
	14.72	1.340	.7208	.4620	.6921	.177	.237
	21.52	1.386	.9159	.3291	.7543	.180	.249
	28.52	1.447	$\bar{3}.0709$	.2414	.8216	.182	.263
	35.52	1.521	.1997	.1826	.8916	.187	.284
	42.34	1.603	.3100	.1441	.7964	.187	.300
100	7.78	1.260	$\bar{2}.3401$	.6966	.6085	.191	.241
	14.72	1.272	.6359	.4376	.6453	.199	.253
	21.52	1.291	.8188	.2920	.6826	.202	.261
	28.52	1.319	.9602	.1887	.7207	.202	.266
	35.52	1.353	$\bar{1}.0750$	.1127	.7595	.199	.269
	42.34	1.392	.1699	.0551	.7968	.196	.273
	49.36	1.44	.2561	.0089	.8368	.191	.275

p is expressed in atmopsheres, v in $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$ and C_v and C_p in $\frac{\text{calories}}{\text{gr.} \times \text{degree}}$.

C_p are platted as functions of p. Values based on Joly's measurements (Table XII.) are included.

C_p Agreement with the Results of Others.—Very little agreement is to be found between the values of C_p here computed and the values of C_p obtained from a plat of Lussana's[33] results. The values of C_p for a pressure of one atmosphere as determined by the direct experiments of Holborn and Austin[42] and by those of Swann[43] and as computed here are included in Table XIV. Excepting for the 100° C. value, the computed results agree very well with the results of Holborn and Austin. At 100° C. the agreement is not good, though a better agreement is to be found with Swann's value for this temperature.

Table XIV.

Values of C_p for CO_2 at atmospheric pressure expressed in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

T	Holborn & Austin	Swann.	Worthing.
0	.203		.202
20		.202	
30	.207		.208
50	.210		.212
100	.216	.221	.228

Causes for Possible Experimental Error.—Realizing early that the values for γ at 100° C. were slightly lower than was expected, special care was taken with the measurements. It is also, of course, an open question whether or not Kammerlingh Onnes's equation, which here bridges an experimental gap from 1 to 50 atmospheres and which here reaches its upper temperature limit of application, correctly represents the interrelations of p, v and θ for this region. The writer can not see how any experimental error in his work might produce this discrepancy. The supposition that the gas in the compression chamber has not all reached the temperature of the bath would lead to a discrepancy in the opposite direction, as would also the fact that a small amount of the gas, that in a portion of the connecting tubes, is at a considerably lower temperature than the bath. The possibility of local cooling next to the plunger during a compression might be thought to explain a part of the discrepancy. But that this is of small consequence is indicated by the good agreement obtained for γ by the rarefaction and by the compression measurements (Table XI.). Moreover, any such experimental error would be effective at the higher pressures, tending to produce too high values for C_v as well as C_p, an effect which is not in evidence in comparing the present results with Joly's (Figs. 9 and 10).

C_v Comparison with Joly's Results.—The attempt to compare the results on C_v computed above with the direct experimental values of Joly[32] has not been as thorough as might be wished due to insufficient data. Joly concluded that the variations of C_v with temperature were very small for densities less than .08 gr./cm.^{3} for the temperature interval 0° C. to 100° C. The fact that his data do not strictly bear out his conclusion was ascribed to the observational inaccuracies entering in his work at the lower densities. This conclusion was accepted in the forming of Table VI. If it is fully accepted, very little agreement is to be found between the writer's values of C_v and those of Joly's. Moreover, it is not compatible with the results of Holborn and Austin and of Swann on C_p at one atmosphere and the ordinarily accepted variations of γ with the temperature for the same pressure. These would require that at atmospheric pressure C_v should increase noticeably with temperature, a variation just the opposite of that found by Joly for the higher pressures. The writer has assumed that the apparent disappearance of a temperature effect with decreasing densities in Joly's results might have been a disappearance preparatory to a reversal of the temperature effect, and has computed from Joly's individual results what the values of C_v would be for certain densities and temperatures if the results were correct. In doing this Joly's equation for C_v at a density of .124 gr./cm.^{3} has been used. For the densities .0800 gr./cm.^{3} and .0456 gr./cm.^{3} values of C_v were obtained by the deriving of an equation holding over a portion of the temperature range in a manner similar to that used by Joly. Other values of C_v were obtained by a quadrature method based on the general principle that

$$C_v = \frac{\partial}{\partial T}\Big[\,\bar{C}_v(100 - T)\Big]_v, \tag{58}$$

where $\bar{C}_v$ is the mean value of C_v between T and 100° C. These results with corresponding values obtained from the writer's work are included in Table XV. The table indicates a fair agreement between the results

TABLE XV.

Corresponding values of C_v as determined by Joly and by Worthing.

T	p	C_v (Joly)	C_v (W.)	p	C_v (Joly.)	C_v (W.)	p	C_v (Joly.)	C_v (W.)
0°	19.4	.194	.193						
30	22.6	.178	.186	36.0	.189	.193	49.0	.208	.205
50	24.6	.170	.181	40.0	.185	.186			
100	29.5	.206	.202	49.0	.200	.192			

p is expressed in atmospheres, C_v in $\dfrac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of Joly thus interpreted and the writer's. As suggested above, insufficient data may account for a part of the actual variations.

Conclusions Regarding C_v and C_p.—For the region considered in CO_2, the following conclusions may be drawn:

1. The isometric heat capacity of CO_2, C_v, at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.
2. For a given temperature C_v generally increases with increasing pressure. The reverse is true for a certain pressure interval at 100° C.
3. There is a good agreement between the results on C_v obtained by the writer and those obtained by Joly.
4. The isopiestic heat capacity C_p at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.
5. For a given temperature C_p increases with increasing pressure.
6. The variation of C_p at 30° C. is such as to be consistent with a theoretically infinite value at the critical point.
7. At atmospheric pressure the computed values of C_p agree well with the experimental values of Holborn and Austin and of Swann.
8. At high pressures the values found using the writer's experimental results are such as to be consistent with results based on Joly's data on C_v.
9. Very little agreement has been found between the writer's results and Lussana's results.

VI. THE FREE-EXPANSION AND JOULE-KELVIN EFFECTS IN CO_2.

Results.—The methods of computation were those detailed in connection with the free-expansion and Joule-Kelvin effects in air. The results are to be found in Table XVI. Results for pressures of 50 atmospheres and higher for 50° C. and 100° C. have been determined by taking the results of Joly on C_v, the individual values being taken from the curves of Fig. 10. A value for both μ and η at the critical point ($p = 72.9$ atmos., $\theta = 304.5°$ K.) has been obtained by Keesom[44] by measuring the $dp/d\theta$ of the vapor tension curve of CO_2 at that point. Theoretically at the critical point of a substance there exists but a single value for $dp/d\theta$. This follows at once from (8), since at this point $(\partial p/\partial v)_\theta = 0$. Consequently we have

$$\mu_c = \eta_c = \left(\frac{d\theta}{dp}\right)_c \tag{59}$$

where the subscript c indicates the critical point values. These values of μ and η are included in Table XVI. The results as functions of the

Table XVI.

Data for and results on μ and η for CO_2. *Results based on K. Onnes's equation and on γ data by Worthing.*

T in °C.	p in Atmos.	$\theta - v\left(\frac{\partial\theta}{\partial v}\right)_p$ in °K.	$\theta\left(\frac{\partial p}{\partial\theta}\right)_v - p$ in Atmos.	μ in deg./atmo.	η in deg./atmo.	$\frac{\Delta W_1}{\Delta W_2}$
0	7.78	48.8	1.12	1.398	1.266	.144
	14.72	87.9	4.44	1.333	1.259	.302
	21.52	125.9	10.62	1.334	1.262	.494
	28.52	161.3	21.52	1.329	1.265	.750
30	7.78	38.3	.76	1.084	.979	.098
	14.72	69.5	2.93	1.051	.978	.199
	21.52	99.7	6.64	1.063	.989	.309
	28.52	128.3	12.51	1.054	.993	.440
	35.52	157.0	21.28	1.059	1.008	.600
	42.34	183.6	33.42	1.061	1.023	.790
	49.36	209.4	51.04	1.048	1.023	1.035
	57.0	235.2	79.67	.995	.985	1.40
50	7.78	33.3	.61	.926	.833	.078
	14.72	60.3	2.27	.901	.827	.154
	21.52	86.5	5.10	.905	.836	.237
	28.52	112.4	9.52	.912	.854	.334
	35.52	136.5	15.65	.914	.868	.440
	42.34	158.8	23.62	.905	.870	.560
100	7.78	24.3	.38	.618	.557	.049
	14.72	44.3	1.41	.587	.537	.096
	21.52	63.9	3.06	.586	.530	.142
	28.52	82.5	5.52	.586	.539	.194
	35.52	100.4	8.82	.591	.553	.249
	42.34	116.7	12.84	.596	.565	.304
	49.36	133.1	17.96	.604	.583	.364
Results Based on C_v Data by Joly and p, v, θ Data by Amagat.						
50	50	183	35.6	.895	.865	.713
	60	212	58.0	.860	.850	.980
	70	240	89.8	.835	.835	1.28
	80	265	145.5	.765	.780	1.82
	90	286	230.0	.655	.670	2.62
100	71.3	190	48.4	.635	.660	.68
	87.8	221	80.2	.585	.615	.92
Results Based on $dp/d\theta$ at Critical Point by Keesom.						
31	72.9	304	416.	.622	.622	5.71

closely to the drawn curves. The variations here are such as would indicate that for good agreement of the results among themselves, the values of γ for the lower pressures should be somewhat less than they have been indicated to be. This is in exact conformity with the indications derived above in considering γ' of (49). However, the smallness pressure and the temperature are platted in Fig. 11. Excepting for the values at zero pressure and at 7.78 atmospheres, the points lie very of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$ for low pressures might well account for the variations in μ and η in such cases.

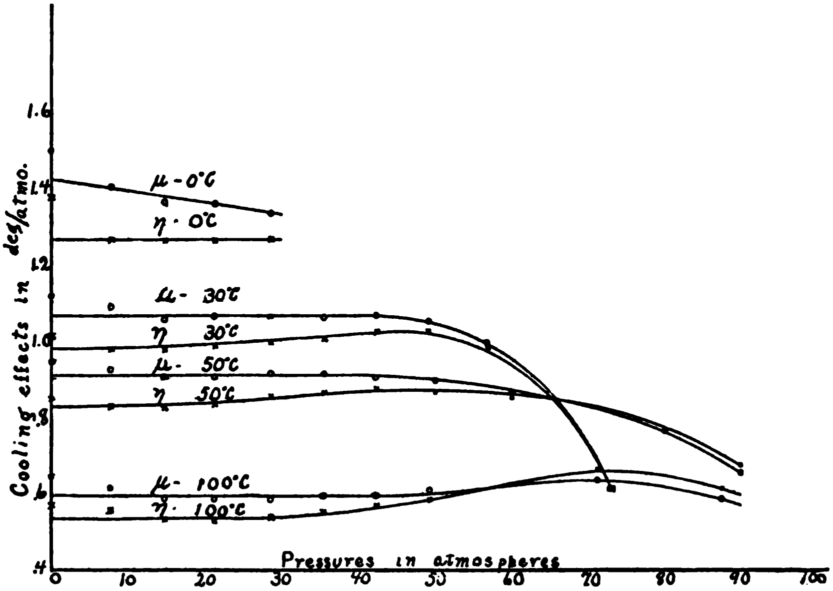


Fig. 11.

Variation of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO_2 with temperature and pressure.

Results based on determinations of

C_v by Joly.. ● ■

γ by Worthing.. ○ ×

$\frac{dp}{d\theta}$ by Keesom.. ■

Results for Low Pressures.—In Fig. 12 there have been platted μ and η as functions of the temperature for the gas under low pressures. There have been indicated also the results of Kester,[14] Joule and Kelvin,[9] Natanson[13] and some other observers. The non-agreement of μ and η at zero pressures with values at the higher pressures led the writer to consider the application of data by Chappuis[45] on the p, v and θ interrelations and data on C_p by Holborn and Austin. Chappuis's results are expressed in equations of the form

$$pv = A + Bp \tag{60}$$

for five different temperatures, − 17.5°, 0°, 20°, 40° and 100° C. A and B are constants. The unit of pressure used is that due to a meter column of mercury, the unit of volume is that occupied by a gram molecule of the gas, at 0° C., under a pressure equal to that due to a meter column of mercury. In a method exactly analogous to that used in obtaining (27) and (28), we get for $p = 0$

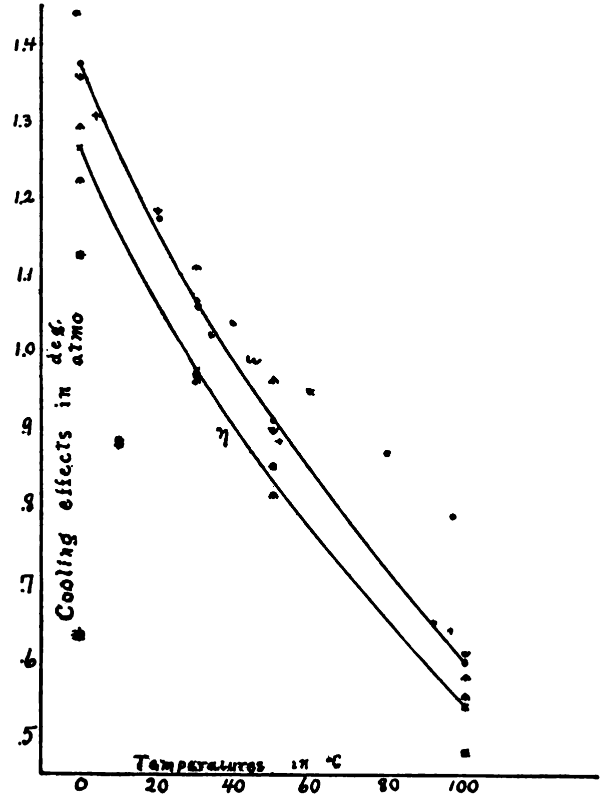


Fig. 12.

Variation with temperature of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO_2 at low pressures.

Determinations of Joule-Kelvin effects	
by Joule and Kelvin	+
by Natanson	∨̇
by Kester	●
from data by Chappuis and by Holborn and Austin	∧̇
from Clausius's equation	◡̇
by Worthing	○
Determinations of free-expansion effects	
by Cazin	#
by Searle	*
from data by Chappuis and by Holborn and Austin	⊡
from Clausius's equation	◠̣
by Worthing	×

$$\mu_0 = \frac{\theta\left(\frac{\partial B}{\partial \theta}\right)_p - B}{C_p}, \tag{61}$$

$$\eta_0 = \frac{\theta\left(\frac{\partial B}{\partial \theta}\right)_p}{C_p - \frac{A_0}{\theta_0}}, \tag{62}$$

where A_0 and θ_0 are the values of A and θ for 0° C. (61) and (62) are based on the assumption that

$$A = A_0\frac{\theta}{\theta_0}, \tag{63}$$

a condition which is necessary if the gas in question is to approach the condition of a perfect gas as the pressure approaches zero. Chappuis's constants do not quite fulfil condition (63). Slight changes were made in his values for A and B, leaving the values for A and B at 0° C. and the values of pv at the unit of pressure unchanged, such that condition (63) was fulfilled. This seems reasonable, in view of the added fact that, of the measurements by Chappuis at three different pressures, the average pressure was about equivalent to that due to a meter column of mercury. Thus changed B is readily and with a great deal of accuracy expressed by the following empirical formula,

$$10^5 B = -906 + 6.87T = .0226T^2. \tag{64}$$

Chappuis's value for A_0 is 1.00906. The values indicated as being based on data by Chappuis and by Holborn and Austin, were obtained under the above named conditions. Some check computations for μ and η at 1 m. of Hg pressure based on quadrature methods and using Chappuis's constants unchanged showed excellent agreement with the values obtained using the modified constants of (63) and (64). To obtain values of C_p at zero pressure Holborn and Austin's data were used in conjunction with the change for one atmosphere indicated by the curves in Fig. 10. The results indicated as being based on Clausius's equation were obtained for zero pressure by a method analogous to that used in obtaining (27), and (28), and (61) and (62). Clausius's[46] equation and the numerical values of the constants are given in (65).

$$p = \frac{R\theta}{v - a} - \frac{c}{\theta(v + b)^2} \tag{65}$$

$$R = .003688,$$
$$a = .000843,$$
$$b = .000977,$$
$$c = 2.0935.$$

The resulting values for μ and η at zero pressure are

$$\mu_0 = \frac{\gamma - 1}{\gamma}\left(\frac{3c}{R^2\theta^2} - \frac{a}{R}\right), \tag{66}$$

$$\eta_0 = \frac{2c(\gamma - 1)}{R^2\theta^2}. \tag{67}$$

The curves of Fig. 9 furnished the desired values of γ. The value found by Searle[8] was obtained through considering the application of Van der Waal's equation. The value by Cazin[7] is an average of the four values .81, .82, .82 and 1.09 deg./atmo. which are obtainable from his results. The method is briefly described in the introduction. The first value is directly obtainable from his results. The other values are obtained indirectly. In obtaining his results for these three cases, Cazin had the larger chamber, into which the gas experimented on expanded from a smaller chamber, partially filled with the gas. In arriving at the above values, the rough assumption was made that the gas freely expanding was that in the smaller chamber in excess of the amount necessary to produce it in a pressure equal to the pressure existing in the larger chamber.

Note Regarding Disagreement of Values at Zero Pressure.—The high values of μ and η for $p = 0$ using Kammerlingh Onnes's equation (Fig. 12), are offset by the results based on the careful work of Chappuis and the work of Holborn and Austin and the results obtained with the aid of Clausius's equation. The difference arises from small variations in the p, v, θ relations. This disagreement might seem to cast doubt upon the values for the higher pressures. This is not necessarily the case, however, for with increasing pressure, as mentioned before, small errors in the p, v, θ relation become less effective due to the relative increase in size of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$.

Internal Work during Expansion.—As in the case with air, it is of interest to consider the relative magnitude of the internal work on expansion when compared with the external work. (35) gives this relation for an infinitesimal, reversible, isothermal expansion. Values of $\frac{\Delta w_1}{\Delta w_2}$ are included in the final columns of Table XVI. The results, excepting the value 5.71 for the critical point, have been platted in Fig. 13. The platted points fall very closely on the smoothed curves. The effects of temperature and pressure are well shown. This plat incidentally shows very plainly the cause for the high values for γ at the higher pressures. In determining the isopiestic heat capacity of a gas, one necessarily must consider the internal work of expansion, a factor which does not enter into the isometric heat capacity. Consequently there are relatively large values of γ, where the values of $\frac{\Delta w_1}{\Delta w_2}$ are relatively large. This relation is further borne outby the striking similarity of the two plats.

Conclusions Regarding and μ, η, $\frac{\Delta w_1}{\Delta w_2}$ *for* CO_2.—The following conclusions for CO_2 for the regions considered may be drawn from the plats of μ, η and $\frac{\Delta w_1}{\Delta w_2}$.

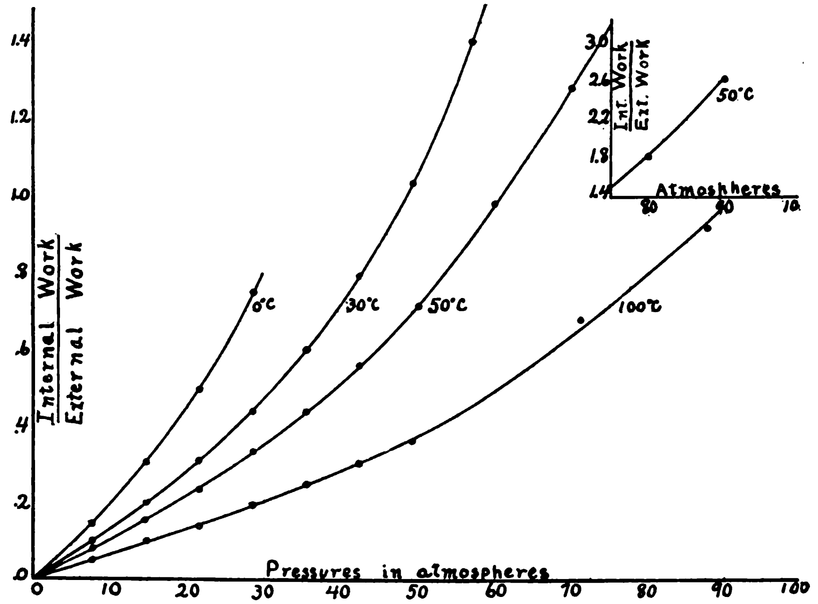


Fig. 13.

Variation with pressure of $\frac{\text{internal work}}{\text{external work}}$ for reversible, infinitesimal, isothermal expansions in CO_2.

Results based on determinations of

C_v by Joly .... ●

γ by Worthing .... ○

1. For pressures up to about 60 or 70 atmospheres the free-expansion effect is less everywhere than the corresponding Joule-Kelvin effect. For the higher pressures the reverse is true.

2. For pressures up to about 60 or 70 atmospheres the values of μ and η decrease with increasing temperatures for the temperature interval 0° to 100° C. For sufficiently high pressures there is a reversal of this temperature effect.

3. μ for a given temperature is approximately independent of the pressure up to about 40 atmospheres. For higher pressures (excepting at 100° C.) it decreases with increasing pressure.

4. η for a given temperature is nearly constant with varying pressure up to about 30 atmospheres. With increasing pressures η first increases slightly, then decreases more rapidly.

5. There is general good agreement among the μ and η determinations based on the different experimental data.

6. The writer's computed values for μ at moderate pressures agree very well with the experimental values of Joule and Kelvin and with the values obtained by using Clausius's equation, but are consistently less than the results of Kester.

7. The writer's values for η show excellent agreement with the values to be computed on making use of Clausius's equation.

8. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ is greater for a given pressure the lower the temperature.

9. The ratio $\frac{\Delta w_1}{\Delta w_2}$ starts with zero values at zero pressure and increases with pressure, reaching a value of 5.71 at the critical point.

VII. SIGNIFICANCE OF A NOTICEABLE RELATION BETWEEN μ AND η FOR AIR AND FOR CO_2.

It is to be noticed that the results for μ and η for air and CO_2 show some marked differences. Among them is the fact that η is greater than μ in air for the region considered, while the reverse is true for a large portion of the region considered in the case of CO_2. A brief discussion of this fact may perhaps bring out the significance of this. Consider Fig. 14 in which *POQ* represents an isothermal platted on a (pv, p) diagram. Consider some gas to be in a state represented by *O* on the diagram and about to be expanded through a porous plug. On the diagram, the path representing the change will evidently proceed from *O* to some point to the left of *mn*,

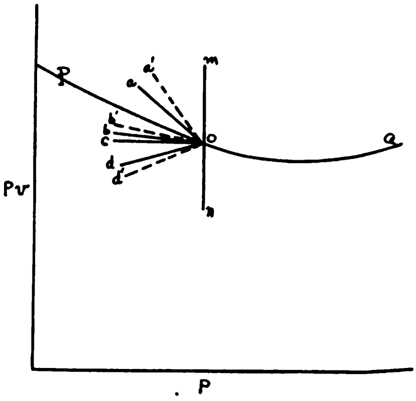


Fig. 14.

an isopiestic through O. In case the path should be along Ob, Oc or Od, cooling of the gas would occur and a positive Joule-Kelvin effect, as in air or in CO_2, would be evidence. In case the path should be along Oa, heating of the gas would occur and a negative Joule-Kelvin effect as in hydrogen would be evidenced. The condition necessarily fulfilled in a porous plug expansion is

$$\Delta\epsilon + \Delta(pv) = 0. \tag{68}$$

The condition necessarily fulfilled in a free-expansion is

$$\Delta\epsilon = 0. \tag{69}$$

According to conditions, for instance whether in Fig. 14 the path proceeds from O into the upper left hand quadrant, along Oc, or into the lower left hand quadrant, we have respectively for the porous plug expansions

$$\Delta(pv) > 0, \quad \Delta(pv) = 0, \quad \Delta(pv) < 0. \tag{70}$$

For these cases we also have respectively

$$\Delta\epsilon < 0, \quad \Delta\epsilon = 0, \quad \Delta\epsilon > 0. \tag{71}$$

In the first case, where the path representing the porous plug expansion proceeds into the upper left hand quadrant and for which $\Delta\epsilon < 0$, the path for a free-expansion, in which $\Delta\epsilon = 0$, lies above that for the porous plug expansion. Hence, taking into account the signs of the effects, the free-expansion effect is less than the Joule-Kelvin effect.

In the second case, where the path representing the porous plug expansion proceeds along Oc and where $\Delta\epsilon = 0$, the path for a free-expansion also proceeds along Oc. Here the two cooling effects are equal.

In the third case, where the path representing the porous plug expansion proceeds from O into the lower left hand quadrant and for which $\Delta\epsilon > 0$, the path for a free-expansion in which $\Delta\epsilon = 0$, lies below that for the porous plug expansion. Here the free-expansion effect is greater than the porous plug effect. The converse of these statements is also true.

In the regions considered in air and in CO_2 we have for the most part portions of isothermals which when represented on diagrams as in Fig. 14 correspond to the portion PO. In air where the Joule-Kelvin and free-expansion effects are both positive and the latter the greater, we have porous plug expansions and free-expansions whose paths would correspond respectively to Od and Od'. For CO_2 at the lower pressures, where the Joule-Kelvin and free-expansion effects are both positive and the latter the smaller, the corresponding paths are *Ob* and *Ob′*. At somewhat higher pressures where the two effects are equal, the corresponding paths coincide and lie along *Oc*. At still higher pressures where the two effects are reversed, we have conditions existing as described above in air.

VIII. Summary.

1. An expression has been developed which shows clearly the relation between the free-expansion effect η and the ratio of the two heat capacities γ of a substance.

2. With the aid of γ data by Koch, $pv\theta$ data by Witkowski and an empirical equation of state by Kammerlingh Onnes, there have been computed values for the free-expansion effect η, the Joule-Kelvin effect μ and the ratio of the internal work to the external work for infinitesimal reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ for air at 0° C. and at $-$ 79.3° C. and for pressures up to 130 atmospheres.

3. With the aid of Kammerlingh Onnes's equation of state, there have been obtained experimentally by Maneuvrier's method values of γ for CO_2 at 0.0°, 31.0°, 50.0° and 98.5° C. and for pressures ranging from about 8 atmospheres to 57 atmospheres.

4. The approximate constancy of a new function γ' where γ' is defined by $pv^{\gamma'}$ = constant—for CO_2 has been pointed out.

5. Values for the isometric heat capacity C_v, the isopiestic heat capacity C_p, μ, η and $\frac{\Delta w_1}{\Delta w_2}$ for CO_2 at 0°, 30°, 50° and 100° C. and for pressures—making use of C_v data by Joly—up to 90 atmospheres have been computed.

6. The results of the present work have been shown to be generally in good agreement with the experimental results of others.

7. A discussion has been presented in which certain characteristics of the expansions of air and of carbon dioxide through a porous plug and into a vacuum are considered.

The conclusions reached regarding the variations of the various quantities considered will be found summarized at the close of the different subdivisions of the present paper.

In conclusion, I wish to express my sincere thanks to Mr. R. E. Miller for care shown in the construction of the apparatus, to Mr. C. E. Guthe, Jr., for efficient aid given in the experimental work, and especially to Dr. K. E. Guthe for his kindly interest and helpful suggestions.

University of Michigan,
Ann Arbor, Mich.,
March, 1911.

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THE MAGNETIZATION OF COBALT AS A FUNCTION OF THE TEMPERATURE AND THE DETERMINATION OF ITS INTRINSIC MAGNETIC FIELD.

By W. W. Stifler.

Introduction.

THOUGH cobalt has always been classed as one of the strongly magnetic metals, its properties do not seem to have been studied with the interest manifested in those of iron and nickel. In spite of the work of E. Becquerel,[1] Plücker,[2] Rowland,[3] Hankel,[4] H. Becquerel,[5] Gaiffe,[6] Trowbridge and McRea,[7] Berson,[8] Bidwell,[9] Ewing and Low,[10] duBois,[11] Fleming, Ashton and Tomlinson,[12] Beattie,[13], and Nagaoka and Honda,[14] until very recently the amount of real numerical data on the magnetic properties of cobalt, even at ordinary temperatures, was very meagre.

Within the last two years several articles have been published which are of great interest from a theoretical point of view. One of these is by P. Weiss[15] and gives the results of work at ordinary temperatures; another is by Weiss and Kamerlingh Onnes[16] and gives the results of their work at very low temperatures. In the investigation described in the first of these papers, the saturation value of the specific intensity of magnetization—that is, the intensity of magnetization per gram—was determined. Weiss found that the law of approach to saturation at 17° C. for cobalt was given by the equation

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$$\sigma = 162\left(1 - 1.11\frac{10^6}{H^2}\right),$$

where σ is the specific intensity of magnetization. By plotting σ as a function of $1/H^2$ and extrapolating he found the saturation value to be 162 at 17° C. These results were confirmed by the work of Droz[1] published at the same time. In the second investigation measurements were taken at temperatures as low as that of liquid hydrogen. The value of σ at these very low temperatures was found to be less than 163.6.

Very recently Weiss[2] has measured the specific susceptibility of cobalt in the temperature interval from 1156° C. to 1302° C. using a method similar to that employed by Curie in his classical researches on the magnetic properties of bodies at high temperatures.[3] This article was published some months after the present investigation was undertaken. Weiss states that the "Curie point" for cobalt is probably in the neighborhood of 1110° C.

The recent developments of the electron theory of magnetism make a knowledge of the saturation value of the intensity of magnetization as a function of the temperature of great theoretical interest and the present investigation was undertaken with the objects:

1. To determine the specific intensity of magnetization at various temperatures up to about 1150° C.; that is, to a temperature somewhat above that at which spontaneous ferro-magnetism disappears.

2. To deduce from these data the value of the intrinsic molecular field of cobalt and the moment of its elementary magnet.

METHOD.

For this purpose, the method used by Weiss[4] seemed best adapted. It consists essentially in observing the throw of a ballistic galvanometer connected in series with a helix placed in a strong longitudinal magnetic field when an ellipsoid of the substance to be tested is suddenly jerked out of the helix. The throw of the galvanometer is then compared with that produced when a known current is made or broken through the primary of a standard helix, the secondary of which is included in the galvanometer circuit. The connections are shown diagrammatically in Fig. 1, where C is the cobalt ellipsoid; H is the induction helix connected in series with the controlling resistance, R', the galvanometer, G, and the secondary, S, of the standard helix; P is the primary of the standard helix; R, the controlling resistance; and A is a carefully calibrated ammeter.

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[1] Archives des Sciences (Geneve), Ser. 4, *29*, pp. 204–224 and 290–309, 1910.

[2] Archives des Sciences (Geneve), Ser. 4, *31*, pp. 5–19 and 89–117, 1911.

[3] Ann. de Chim. et de Phys., Ser. 7, *5*, pp. 289–405, 1895; Œuvres, pp. 232–334.

[4] Journal de Physique, Ser. 4, *9*, pp. 373–393, 1910; Archives des Sciences (Geneve), Ser. 4, *29*, pp. 175–203, 1910.

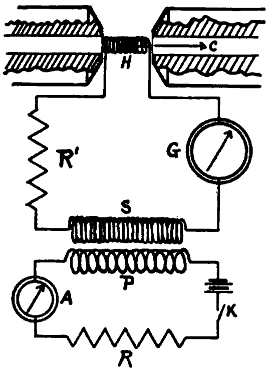

Fig. 1.

The formulæ for σ and I by this method are easily shown to be

$$\sigma = \frac{n_1 n' A(1 - d_1^2/2l_1^2)}{10mn(1 - d_2^2/2l_2^2)} \cdot \frac{I'}{d'} \cdot d = K \cdot d,$$

and

$$I = \frac{n_1 n' A\ (1 - d_1^2/2l_1^2)}{10 Vn\ (1 - d_2^2/2l_2^2)} \cdot \frac{I'}{d'} \cdot d = K'd.$$

where A = area of cross section of primary of standard helix.
n_1 = number of turns per cm. on primary.
N' = total number of turns on secondary.
l_1 = length of primary.
d_1 = diameter of primary.
n = number of turns per centimeter on H.
l_2 = length of H.
d_2 = diameter of H.
m = mass of C.
V = volume of C.
d = deflection of galvanometer when C is jerked out of H.
d' = deflection when current is made or broken through primary.
I' = current in amperes through primary.

The advantage of using σ rather than I lies in the fact that σ is independent of changes in density or volume due to changes in temperature. The value of the field H inside the ellipsoid for an external field of H_0 is[1]

$$H = H_0 - LI,$$

where L is the demagnetizing factor of the ellipsoid.

EXPERIMENTAL DETAILS.

Magnet.—The magnetic field was obtained by means of a large electromagnet of the duBois type. The core was approximately 10 cm. in diameter. For this work it was equipped with a pair of conical pole pieces 2.5 cm. in diameter at the smaller end. A hole 2.1 cm. in diameter was drilled through these to permit the ellipsoid to be withdrawn. The magnet would carry 25 amperes for several minutes without undue heating. For each air-gap used, the strength of the field at the center was determined by means of a flip coil and ballistic galvanometer calibrated by comparison with a standard helix. The field was also measured with a magnetic balance made by Weber in Zurich and practically identical with the one described by Weiss.[1] The results obtained by the two methods were in close agreement. For convenience, the value of the field for currents from 2 to 25 amperes was determined by steps of two or three amperes. From these data curves were plotted giving H as a function of the current, the scale being such that 1 cm. was equivalent to 100 or 200 lines per square centimeter.

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[1] Maxwell, Treatise on Electricity and Magnetism, 3d Ed., Vol. II., §437–438, pp. 66–69.

Galvanometer.—The galvanometer used was a Leeds and Northrup type H instrument. It had a resistance of 26.4 ohms, a ballistic sensibility of 45.6 mm. per microcoulomb on open circuit with a scale distance of 50 cm., and a period of 12.7 seconds on open circuit. The scale used had 500 divisions in a length of 25 cm. and was made by photography from a very accurate 50 cm. scale. The sensitiveness was further increased by placing the scale at a distance of approximately three meters. With this arrangement the "throw" could be read accurately to 0.5 of a scale division or even less. As the instrument as used was on closed circuit, it was practically aperiodic, and its sensitiveness was considerably reduced.

Heating Apparatus.—The induction helix was used as the core around which was built up a small electric furnace to give the necessary temperatures. For various reasons two separate pieces of apparatus were built, one for the lower temperatures, the other for the higher temperatures.

Up to 550° C. the apparatus shown in section in Fig. 2 was used. The induction helix was of No. 30 bare copper wire wound on a hard glass tube. The wire was held in place by cæmentium and, where necessary, fibers of asbestos were worked in between the individual turns. There were 89 turns in a length of 4 cm.

The heating coils were of No. 16 german silver wire and were insulated from the induction helix by a glass tube as shown. In order to decrease the temperature gradient at the center of the induction helix, two heating coils were used. The inner one was wound as regularly as possible, while the outer one was wound closely at the ends but with the turns much farther apart at the middle. The two coils were separated from each other by mica. In order to reduce the magnetic effect of the heating currents, the two coils were always connected so that they opposed each other magnetically. By properly adjusting the currents in the two coils, the temperature at the center of the helix could be made constant to within 2° C. over a distance of 10 to 15 mm. The coils were packed in loose asbestos, and the whole apparatus was covered with asbestos board.

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[1] Journal de Physique, *36*, pp. 432–435, 1907. See also L'Eclairage Electrique, *24*, pp. 257–266, 1900, and Journal de Physique, *29*, pp. 383–390, 1900.

Owing to the fact that at the higher temperatures saturation is reached at lower fields, the apparatus used for temperatures above 550° C. was

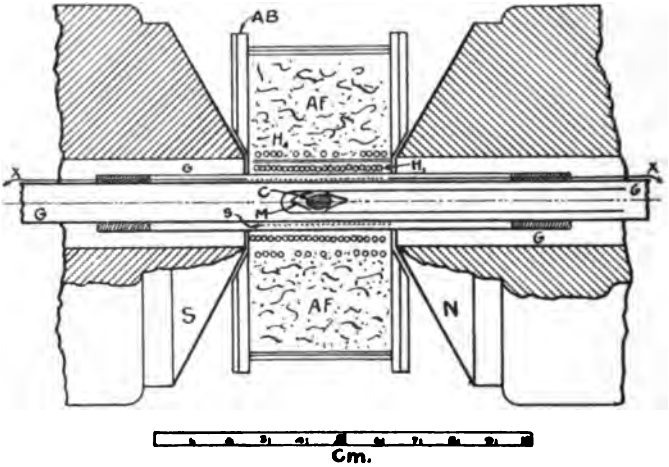

Fig. 2.

S, induction helix; H_1, primary heating coil; H_2, secondary heating coil; *NS*, magnet; *C*, cobalt ellipsoid; *AB*, asbestos board; *AF*, asbestos fiber; *GG*, glass tubes; *M*, mica; *XX*, galvanometer circuit.

somewhat larger though of similar design. The core of the induction helix was a clear quartz tube. The helix was of No. 30 bare platinum wire wound in two layers separated from each other by mica. The individual turns were separated from each other by asbestos yarn. Though the insulating power of this broke down considerably above 1000° C., actual tests showed that this did not introduce any appreciable error.

The heating coils were of No. 13 nickel wire and were separated from the helix by a tube of fused silica. Since nickel loses its magnetic properties at 360° C., no error was introduced by its use. The primary heating coil was wound in two layers. Asbestos yarn was used to separate the individual turns, while the layers were insulated from each other by mica. The secondary heating coil consisted of one layer and was wound as in the other apparatus.

Calcined magnesia contained in a porcelain ring was used as an heat insulator next to the coils. Outside of this a layer of magnesia packing such as is used for high pressure steam pipes was used. The whole apparatus was covered with asbestos board. It is shown in section in Fig. 3. The heating coils on this apparatus burned out several times during the course of the experiments but they were rewound and the apparatus rebuilt in substantially the same way each time. The induction helix was not injured in any way.

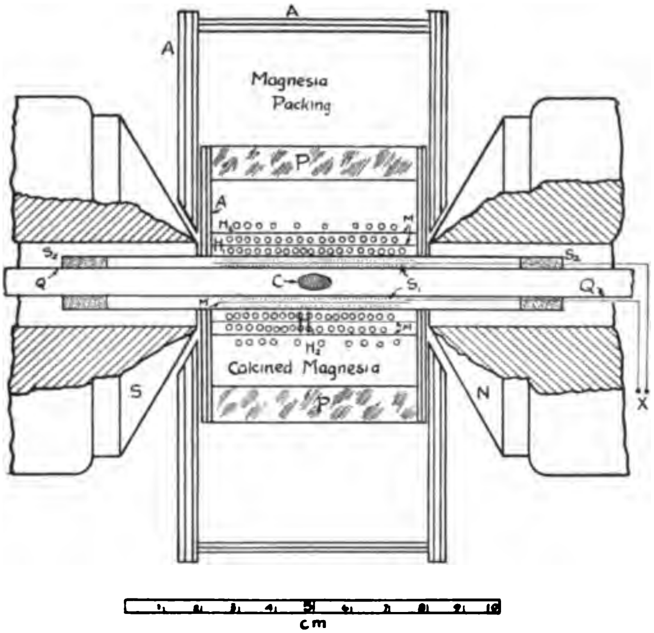

Fig. 3.

S_1, induction helix; S_2, fused silica tube; H_1, primary heating coil; H_2, secondary heating coil; M, mica insulation; A, asbestos board; P, porcelain ring; Q, quartz tube; X, galvanometer circuit.

Temperature Measurements.—Temperatures were measured with a thermocouple. A Wolff potentiometer and Weston standard cell were used to measure its e.m.f., and the resistance in the galvanometer circuit was adjusted so that the instrument read directly to one microvolt. The method of reading and calibration was essentially that described by Clement and Egy.[1] For temperatures between 100° C. and 420° C., a copper-platinum thermocouple was used. As this has an inversion point at about 60° C., it was not used below 100° C. It was calibrated by the boiling point of water, the freezing point of zinc, and by several intermediate points lying between 120° C. and 250° C. which were determined by comparison with a carefully calibrated mercury thermometer. The temperatures were read from the corresponding e.m.f.'s by a calibration curve plotted to such a scale that 1 mm. corresponded to 1° C.

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[1] Univ. of Ill. Eng. Exp. Station Bulletin No. 36, 1909.

For temperatures above 420° C., a platinum platinum-rhodium couple was used. This was calibrated at the freezing points of zinc, silver, and copper. From these three points the three constants of the standard parabolic equation were calculated. The couple as used was easily sensitive to 1 microvolt—equivalent to about 0.1° C.—at 1100° C. The temperatures as read from either couple are probably accurate at 1° C.

Preparation and Mounting of the Ellipsoids.—The first samples of cobalt obtained were in the form of small lumps 3 or 4 mm. in diameter. Several attempts were made to fuse these into a button, using first a small assay furnace and later a coke furnace. These attempts proved futile, owing to the very high melting point of cobalt—1489.8° C.

After one or two preliminary trials, a button weighing about 200 grams was prepared from the oxide by the Goldschmidt process. From this two rings were turned and tested by the ring method. The tests on the larger ring—No. 1—gave values of B of only about one tenth the magnitude to be expected. Annealing for several hours at white heat improved this decidedly, though the results were still only about one third of the accepted values. The smaller ring—No. 2—gave similar results without being annealed. Analysis showed that these samples contained about 1 per cent. of aluminum.

One hundred grams of cobalt in rectangular sheets about 6 cm. × 10 cm. × 0.05 cm. were then obtained from Kahlbaum through Eimer and Amend. Tests on a ring—No. 3—made by building up five layers of this showed that its magnetic properties were excellent (see Fig. 4).

To get this material into a form from which ellipsoids could be ground, it was necessary to fuse it into a button or rod. At first this was accomplished by means of a vertical platinum resistance furnace, using a maximum power consumption of approximately 2,200 watts. A No. 0 black lead crucible, lined with a paste of 98 per cent. magnesite and 2 per cent. bone ash, was used. After the lining was thoroughly dry, a charge of about 20 grams of metal was put in and this was covered with a layer of borax glass. After several hours the cobalt fused, giving a very homogeneous button about 2 cm. in diameter and 0.6 cm. thick.

An attempt to repeat the process resulted in burning out the furnace before the cobalt was entirely fused. However one piece was obtained from which it was possible to turn an ellipsoid.

After considerable practice it was found possible to prepare the material by melting it in a fused silica tube held in an arc. Owing to the impossibility of securing anything like uniform heating over even a short distance, it was only with great difficulty that two or three rods approximately 0.5 cm. in diameter and 1.0 cm. to 1.2 cm. long were obtained by this method.

The ellipsoids were ground from the rods on a Landis Universal Grinder, using an alundum wheel with a properly shaped rim. After grinding, the accuracy of the shape was tested and found to be satisfactory by projecting the enlarged shadow of the ellipsoids with an Edinger Drawing Apparatus.

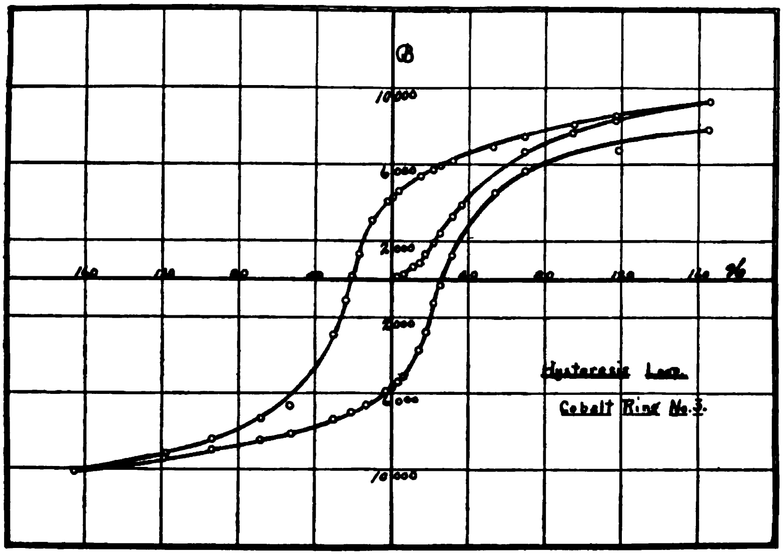

Fig. 4.

In all, five ellipsoids of revolution, approximately 1 cm. long and 0.45 cm. in diameter, were prepared. Complete sets of data, however, were carried out for only two. The ellipsoids were distinguished for convenience as *A*, *B*, *C*, *D*, and *E*. The method of preparing each is given below, and a summary of their dimensions is given in Table I.

A—made from first melting in resistance furnace. Cross-section very accurate.

B—made from the same button as *A*. Not quite as perfect cross-section as *A*.

C—made from rod prepared by melting the metal in fused silica tube held in arc. Cross-section fairly accurate.

D—made from sample melted in silica tube in arc. Cross-section fairly accurate.

E—made from second melting in resistance furnace. Cross-section fairly accurate except for very slight pit near one end.

TABLE I.

	Length.	Mean Diam.	Mass.	Spec. Grav.	Volume by		e	L
					Displac. of Water.	Calculation.		
A	0.9965	0.4475	0.8633	8.25	0.1047	0.1045	0.8934	1.9385
B	0.9330	0.4480	0.8412	8.24	0.1021	0.0981	0.8770	2.0890
C	0.9370	0.4110	0.6804	8.80	0.0773	0.0829	0.8986	1.8888
D	0.9960	0.4430	0.8275	8.74	0.0947	0.1023	0.8956	1.9177
E	0.9920	0.4250	0.8528	8.73	0.0977	0.0938	0.8992	1.8817

In some of the later work, *C* and *E* became more or less oxidized. In each case the oxide was carefully removed with fine emery cloth and the specimen was carefully polished with crocus cloth and weighed. Measurements showed that the shape of the ellipsoids was not altered appreciably by this process.

The reason for the low specific gravity of *A* and *B* is unexplained as yet.

A chemical analysis of the original material showed that it was 100 per cent. pure, with the possibility of a trace of nickel.

For temperatures below 420° C., the ellipsoids were mounted in glass tubes sealed at one end. The thermocouple was inserted through the other end and the junction was separated from the cobalt by a thin layer of mica. As a rule the junction was about one third of the total length of the ellipsoid from the end. For temperatures above 300° C. the end of the tube through which the thermocouple was inserted was sealed with sealing wax, and the whole tube was exhausted and sealed to avoid oxidation of the ellipsoid.

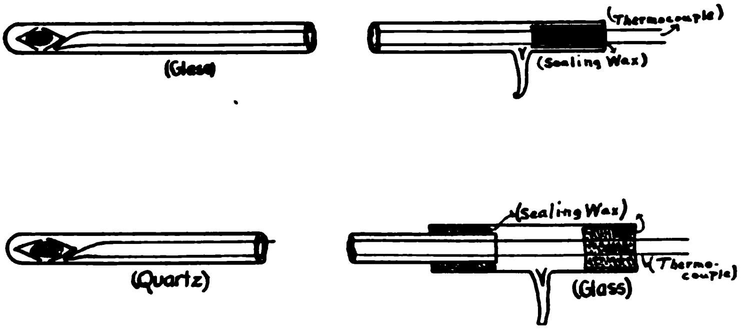

Fig. 5.

For temperatures above 420° C. a clear quartz tube was used to hold the ellipsoid. A glass tube was joined to the open end of this for convenience in exhausting. No particular difficulty was experienced in making the joints air tight with sealing wax, but at the higher temperatures the quartz devitrified upon prolonged heating and the end became "chalky." In this condition it would admit air and in one or two instances as noted above the specimens were oxidized in attempting to carry out a second set of readings. Eventually it was found necessary to re-seal the end of the tube and exhaust the tube anew after each set of readings. Fig. 5 shows the two methods of mounting.

Procedure in Taking Readings.

The general method of taking readings was as follows. The furnace was heated for several hours until thermal equilibrium was established. It was found necessary to draw the heating currents from a large storage battery as the variation of 0.1 ampere caused a very appreciable change in temperature. For the higher temperatures heating currents of 15 to 20 amperes were used. When everything had reached a steady state, the tube containing the ellipsoid and thermocouple was inserted. The position of the tube to bring the ellipsoid into the center of the helix was approximately determined by throwing on the magnetic field for a moment. The tube was then moved by steps of 2 to 5 mm. along the helix, and readings of the temperature at each position were taken after sufficient time had elapsed for the cobalt to take up the temperature of its surroundings. As there is usually comparatively little lag in the readings of a thermocouple, the fact that sometimes as many as twelve or fifteen minutes were required before its readings became constant indicated that the thermocouple was registering the actual temperature of the cobalt. Usually it was possible to adjust the heating currents so that a change of a centimeter in the position of the cobalt produced a change of only 2° or 3° in the readings of the thermocouple. At the lower temperatures it was possible to do much better than this. Under these circumstances, the assumption that the temperature of the ellipsoid was uniform to at least 1° C. seemed justifiable.

The ellipsoid was placed in the position indicated as that at the highest temperature, and the tube was marked so that it was possible to replace it exactly in this position. When the ellipsoid had reached thermal equilibrium, the reading of the thermocouple was taken, the magnetic field was thrown on, and the deflection of the galvanometer when the ellipsoid was jerked out of the helix was noted. The magnetic field was then thrown off and the ellipsoid was replaced in position and allowed to regain its former temperature. As a rule, three readings were taken at each field strength and the mean of the deflections was used in calculating I and σ. At the lower temperatures these readings usually agreed to half a scale division in two hundred or more. At the higher temperatures they were not so great and the agreement was not quite so good. However the readings as a whole were very consistent even under these circumstances, usually agreeing with each other to within 1 per cent. or at most 2 per cent. up to 900° C. The reading of the thermocouple was taken each time just before the ellipsoid was withdrawn, and—as a rule—these readings were not allowed to differ by more than 15 microvolts, corresponding to 1.5° C., during a set of readings. At the very high temperatures where the cobalt was especially sensitive to changes of temperature, the variation was made even less. The mean of the thermo-couple readings was used in calculating the temperature.

After nearly every set of readings, the galvanometer was calibrated by means of the standard helix. The current, I', for this purpose was read by a Siemens and Halske milliammeter which had been calibrated with a standard ohm coil and potentiometer. For temperatures up to 1000° C., the values of I'/d' remained practically constant and the mean value was used in calculating σ.

The magnetic fields used ranged from 1,600 gausses to 6,900 gausses for the lower temperatures, giving fields of from 800 gausses to 5,000 gausses inside the ellipsoids. As these were insufficient to produce saturation below 350° C., the saturation values were determined by an extrapolation similar to that of Weiss mentioned above. As neither σ and $1/H$ nor σ and $1/H^2$ gave a straight line, both were plotted and the mean of the values was used. The results at these lower temperatures were not used in the theoretical deductions so that extreme accuracy in the extrapolated results is not important. Above 350° C. saturation could be reached with the fields used, and at the higher temperatures fields as low as 3,500 gausses produced saturation. The values of the magnetic field were corrected for the magnetic effect of the heating coils whenever this effect was appreciable.

In the interval between 1050° C. and 1100° C. it was very difficult to obtain consistent readings, as a very slight change in temperature produced a marked change in σ. At these higher temperatures also thermoelectromotive effects in the galvanometer caused some difficulty, rendering the zero of the galvanometer somewhat uncertain at times and often causing it to drift steadily in one direction. These difficulties were remedied in large measure by keeping the junctions of the platinum leads from the helix and the copper connecting wires at 0° C.

DATA.

The data obtained for ellipsoids C and E are summarized in the following tables. Tables II. and III. give the values of H and σ as observed at various temperatures, and the values of σ_∞. Table IV. gives a summary of this. Fig. 6 shows the method of determining σ_∞ below 400° C. by extrapolation. The extrapolated values are probably accurate to 1 per cent. Curve A in Fig. 7 shows σ as a function of the temperature. The close agreement between the results for ellipsoids C and E argues for the accuracy of the data.

From the data we can also calculate B and draw magnetization curves for high fields at various temperatures. Several of these curves are shown in Fig. 8.

THEORETICAL CONSIDERATIONS.

In his article upon the magnetic properties of bodies at high temperatures to which reference was made above, Curie called attention to the

TABLE II.

Ellipsoid C.

22° C.		120° C.		235° C.		307° C.		414° C.	
H	σ	H	σ	H	σ	H	σ	H	σ
725	102.4	713	103.0	625	108.4	500	115.9	460	119.2
1,955	139.6	2,154	114.2	1,984	149.2	1,980	149.6	2,055	145.8
2,985	149.1	3,031	151.5	3,026	151.8	3,060	149.9	3,135	146.3
3,450	153.2	3,774	153.5	3,816	152.5	3,825	150.4	3,930	146.4
3,955	154.6	4,200	153.3	4,386	152.8	4,425	150.4	4,515	146.4
4,270	155.2								
σ_∞[1] = 161.0		σ_∞[1] = 158.5		σ_∞[1] = 154.0		σ_∞[1] = 151.0		σ_∞ = 146.4	
542° C.		698° C.		874° C.		991° C.		1043° C.	
H	σ	H	σ	H	σ	H	σ	H	σ
445	120.2	140	87.5	215	83.4	370	72.3	770	46.4
2,160	139.9	855	124.1	1,300	97.9	1,680	72.1	2,070	47.5
3,250	139.6	1,620	124.3	2,015	97.9	2,385	73.1	2,780	49.1
4,015	140.2	2,115	125.2	2,510	98.7	2,880	73.3	3,290	48.9
4,610	140.0	2,400	124.9	3,915	97.9	3,335	71.9	3,680	49.5
σ_∞ = 140.2		σ_∞ = 125.2		σ_∞ = 98.7		σ_∞ = 73.3		σ_∞ = 49.5	
1065° C.		1082° C.		1104° C.		1152° C.			
H	σ	H	σ	H	σ	H	σ		
1,165	21.4	3,250	6.0	1,400	1.3	1,370	?		
2,400	26.8			2,400	1.9	2,380	?		
3,060	30.0			3,050	2.6	3,090	?		
3,570	29.7					3,390	?		
4,010	29.4								
σ_∞ = 30.0		σ_∞ = 6.0		σ_∞ = 2.6(?)		σ_∞ = ?			

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[1] By extrapolation from curves.

Table III.

Ellipsoid E.

22° C.		127° C.		232° C.		300° C.		415° C.		590° C.	
H	σ	H	σ	H	σ	H	σ	H	σ	H	σ
490	66.6	876	94.3	720	103.9	540	114.6	650	108.9	690	106.8
1,285	104.6	2,190	138.6	2,050	147.0	2,175	145.6	2,160	142.2	2,305	132.7
2,575	134.2	3,135	147.1	3,115	148.3	3,140	146.8	3,240	141.6	3,385	133.0
3,260	142.6	3,905	148.9	3,930	149.6	3,970	146.8	3,990	142.6	4,155	133.4
4,065	148.3	4,225	149.5	4,930	149.0	4,505	147.3	4,625	141.2	4,760	132.9
4,445	149.6										
σ_∞[1] $= 161.0$		σ_∞[1] $= 154.0$		σ_∞[1] $= 150.5$		σ_∞[1] $= 148.0$		$\sigma = 142.3$		σ_∞[1] $= 133.1$	

687° C.		867° C.		1029° C.		1057° C.		1113° C.		1144° C.	
165	81.2	200	78.7	710	53.0	850	34.7	3,800	3.5	1,420	?
830	121.4	1,210	97.3	1,850	57.8	2,750	38.4			2,440	?
1,515	121.9	1,950	96.3	1,590	56.8	3,185	38.4			3,360	?
2,055	122.0	2,450	96.3	3,160	53.1						
2,450	122.5	2,850	97.5	3,570	53.5						
$\sigma_\infty = 122.5$		$\sigma_\infty = 97.5$		$\sigma_\infty = 57.0$		$\sigma_\infty = 38.4$		$\sigma = 3.5$		$\sigma = ?$	

Table IV.

Saturation value of σ as a function of the temperature.

Ellipsoid *C.*		Ellipsoid *E.*		Ellipsoid *C.*		Ellipsoid *E.*	
Temp.	σ_s	Temp.	σ_s	Temp.	σ_s	Temp.	σ_s
22°	161.0	22°	161.0	874°	98.7	867°	97.5
120°	158.5	127°	154.0	991°	73.3	1,029°	57.0
235°	154.0	232°	150.5	1,043°	49.5	1,057°	38.4
307°	151.0	300°	148.0	1,065°	30.0	1,113°	3.5
414°	146.4	415°	142.3	1,082°	6.0	1,144°	?
542°	140.2	590°	133.1	1,104°	2.2		
698°	125.2	687°	122.5	1,152°	?		

similarity between the curves showing I as a function of the temperature for iron and nickel on the one hand, and the curves showing the relation between the density of a vapor and the temperature on the other hand. Langevin[2] a little later worked out on the electron theory a mathematical theory of paramagnetism based upon the assumption that the molecules of a paramagnetic substance obey the gas law. Weiss[3] extended this theory to explain the phenomena of ferromagnetism by the aid of the analogy pointed out by Curie. The sudden increase of density when a vapor liquefies is due to the fact that an enormous internal pressure is

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[1] By extrapolation from curves.

[2] Ann. de Chim. et de Phys., Ser. 5, *8*, pp. 70–127, 1905.

[3] Journal de Physique, *36*, pp. 661–690, 1907.

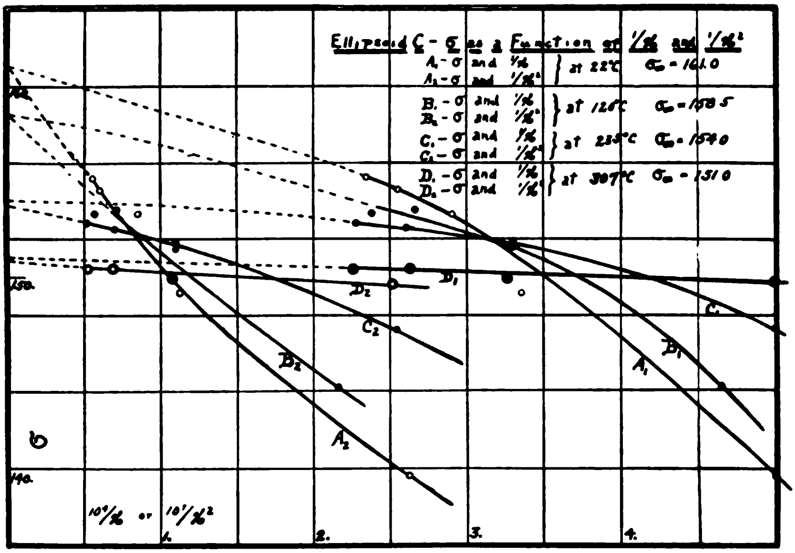
Ellipsoid C - σ as a Function of 1/H and 1/H²
A₁ - σ and 1/H, A₂ - σ and 1/H² } at 22°C σ∞ = 1610
B₁ - σ and 1/H, B₂ - σ and 1/H² } at 126°C σ∞ = 1585
C₁ - σ and 1/H, C₂ - σ and 1/H² } at 235°C σ∞ = 1540
D₁ - σ and 1/H, D₂ - σ and 1/H² } at 307°C σ∞ = 1510
160
150
140
σ
10/H or 10⁷/H²
1.
2.
3.
4.
A₁
A₂
B₁
B₂
C₁
C₂
D₁
D₂

Fig. 6.

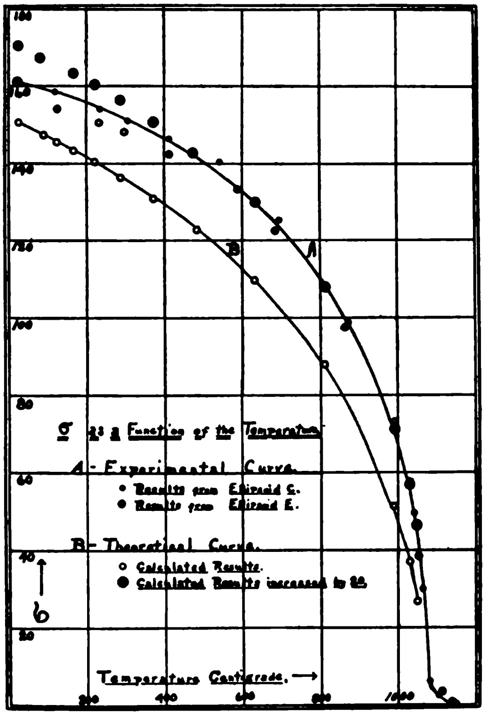
σ as a Function of the Temperature
A - Experimental Curve.
• Results from Ellipsoid C.
● Results from Ellipsoid E.
B - Theoretical Curve.
○ Calculated Results.
● Calculated Results increased to 20.
A
B
180
160
140
120
100
80
60
40
20
σ ↑
Temperature Centigrade. ⟶
200
400
600
800
1000

Fig. 7.

suddenly brought into play in addition to the external pressure. Similarly Weiss explained the fact that the ferromagnetic properties suddenly appear when the temperature is lowered below a certain critical temperature by assuming that a strong molecular field is suddenly made operative. This field is due to the action of the molecules upon each other and is called by Weiss the "intrinsic molecular field." Of course the analogy is not perfect for if it were we should expect the pressure-density curves at constant temperature to show the phenomenon of hysteresis. Weiss has calculated the value of this intrinsic field for iron, nickel, and magnetite. Kunz[1] has extended this work by calculating the moments of the elementary magnets.

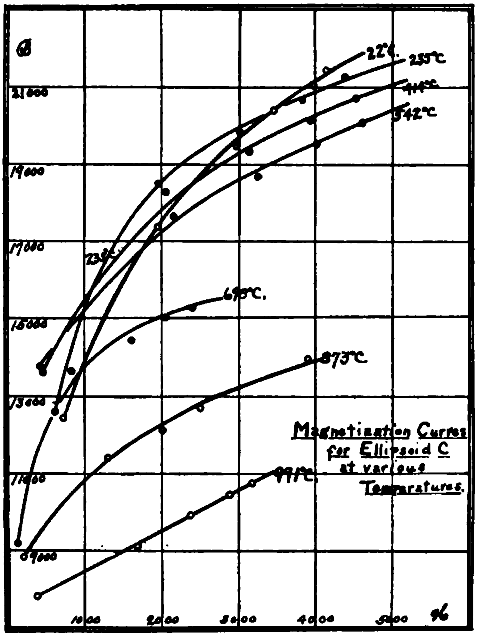

Fig. 8.

Before outlining the theory as developed by these investigators, the terms diamagnetic, paramagnetic, and ferromagnetic as used in this article will be defined.

Diamagnetic substances are those in which the induced polarity opposes that of the inducing field.

Paramagnetic substances are magnetized feebly in the direction of the magnetizing field. The susceptibility is independent of the field strength and is inversely proportional to the absolute temperature according to Curie.

Ferromagnetic substances are very strongly magnetized in the direction of the magnetizing field. The susceptibility is a very complicated function of the field strength and the temperature. The phenomena of hysteresis are characteristic of ferromagnetic substances.

The phenomena of diamagnetism are accounted for by assuming that each atom contains at least one electron revolving in an orbit which lies wholly within the atom. The orbits of the electrons are so arranged that their external moment is zero. Since temperature affects the molecule rather than the atom, the purely diamagnetic properties should be independent of the temperature. It is probable that even the paramagnetic and ferromagnetic bodies also contain electronic orbits which give them diamagnetic properties, but the effect is masked by the stronger opposing phenomena.

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[1] Phys. Rev., *30*, pp. 359–370, 1910.

In the paramagnetic and ferromagnetic bodies, the revolving electrons are so arranged that there is no resulting external moment. Curie[1] showed experimentally for a number of paramagnetic bodies that the paramagnetic susceptibility, $k = I/H$, is inversely proportional to the absolute temperature. This is known as Curie's Law. Langevin, in his article to which reference has already been made, has given a theoretical deduction of this law. Though some very recent experimental results[2] seem to contradict Curie's Law, still on the whole it agrees with the experimental facts in a large number of cases.

The present theory as developed by Langevin, Weiss, and Kunz may be outlined as follows. In a gas at uniform temperature, not subject to the action of gravity, the density is uniform throughout. If gravity is suddenly allowed to act upon the gas, a rearrangement of the molecules occurs; the lower layers of the gas become more dense, and the temperature of the gas rises, due to the fact that a certain amount of potential energy has been converted into kinetic energy—*i. e.*, into heat. The change of pressure with height after equilibrium is established is now given by the familiar exponential law

$$p = p_0 e^{-\rho_0 x / p_0},$$

where p_0 and ρ_0 are the pressure and density respectively at the lowest layer, and x is the height. This law has been generalized by Boltzmann[3] in the form

$$p = p_0 e^{W/RT},$$

where W is the change in the potential energy per unit distance and T and R are respectively the absolute temperature and the universal gas constant.

The arrangement of the molecules in a paramagnetic substance when not under the influence of an external magnetic field is exactly analogous to that of the gas molecules when not under the influence of gravity, and the rearrangement caused by the action of a uniform magnetic field will follow an exactly similar law. The number of molecules, dn, the directions of whose axes are included in an elementary solid angle, $d\omega$, will therefore be given by

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[1] Ann. de Chim. et de Phys., Ser. 7, *5*, pp. 289–405, 1895; Œuvres, pp. 232–334.

[2] du Bois and Honda, Konink. Akad. Wetensch., Amsterdam, Proc. *12*, pp. 596–602, March, 1910.

[3] Vorlesungen über Gas-Theorie, 1 Teil, p. 136.

$$dn = Ke^{W/RT} d\omega, \tag{1}$$

where K is a constant. The potential energy of an elementary magnet of moment M whose axis makes an angle Φ with a uniform magnetic field H is

$$W = HM \cos \Phi.$$

But

$$d\omega = 2\pi \cdot \sin \Phi \cdot d\Phi.$$

Substituting this value and integrating from 0 to π we have

$$n = \frac{4\pi K}{a} \sinh a, \tag{2}$$

where

$$a = \frac{HM}{RT}.$$

This result assumes that the resulting intensity of magnetization is in the same direction as H. In general this will not be the case. If Φ is the angle between H and I we have

$$dI = M \cos \Phi \, dn$$

and

$$I = \int_0^\pi M \cos \Phi \, dn.$$

Substituting the value of dn from (1) and integrating, and then substituting the value of K from (2) we have

$$I = nM \left(\frac{\cosh a}{\sinh a} - \frac{1}{a} \right),$$

where n is the number of molecules in unit volume. Since it is the thermal agitation of the molecules which opposes the action of H, if there were no thermal agitation—*i. e.*, if the substance were at absolute zero—the intensity of magnetization would be a maximum and we would have

$$I_m = nM.$$

Hence

$$I = I_m \left(\frac{\cosh a}{\sinh a} - \frac{1}{a} \right), \tag{3}$$

Since

$$a = \frac{MH}{RT},$$

this gives

$$I = I_m \cdot f\left(\frac{H}{T}\right).$$

For paramagnetic substances, a is very small—much less than unity. For values of a^2 less than π^2, $\frac{\cosh a}{\sinh a} - \frac{1}{a}$ can be developed into a convergent series as follows:

$$\frac{\cosh a}{\sinh a} - \frac{1}{a} = \frac{1}{3}a - \frac{2}{90}a^3 + \frac{4}{45\cdot 42}a^5 \cdots$$

For values of a less than 0.7, the terms of this series involving higher powers of a than the first are negligible, and we have

$$\begin{aligned} I &= \frac{a}{3}I_m, \\ &= \frac{M^2nH}{3RT}, \\ &= kH. \end{aligned}$$

where k is constant for constant temperature. k is the paramagnetic susceptibility and is seen to be inversely proportional to T, as found by Curie experimentally.

In the case of ferromagnetic substances we have, in addition to the external field, an internal or molecular field, H_m. If this field acted alone, the intensity of magnetization would be proportional to it and we would have

$$H_m = NI,$$

and

$$\begin{aligned} a &= \frac{MH}{RT}, \\ &= \frac{MNI}{RT}. \end{aligned}$$

Whence

$$I = \frac{aRT}{MN}, \tag{4}$$

where N is the factor of proportionality. Equation (4) shows that at any given temperature I is proportional to a.

For any temperature below that at which the spontaneous ferromagnetism disappears, the value of I must satisfy both equations (3) and (4). Plotting equation (3) we have the curve OCA of Fig. 9, while equation (4) gives the straight line OA. Obviously the values of I corresponding to the origin and to the point A satisfy (3) and (4) simultaneously. The value for the origin is for $I = 0$. Hence the value of I which we wish is that for the point A.

The line OA corresponds to some particular temperature T, and as T varies, OA rotates about the point 0. If Θ denotes the temperature at which the spontaneous ferromagnetism disappears, the tangent to the curve at the origin corresponds to $T = \Theta$.

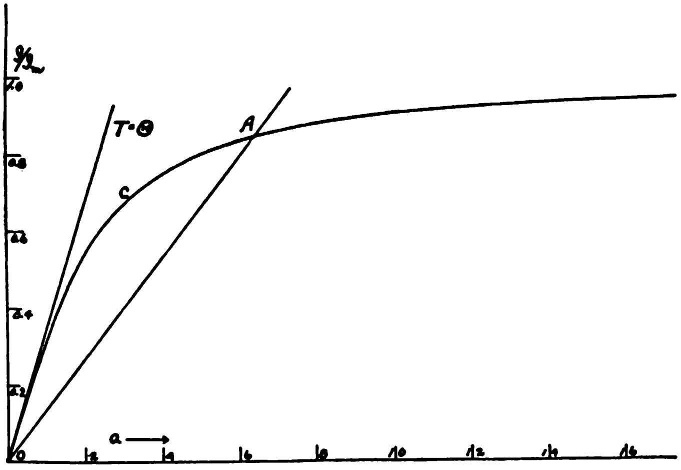

Fig. 9.

From a knowledge of the properties of a body in the neighborhood of Θ it is possible to calculate H_m, the intrinsic molecular field, and M, the moment of the elementary magnet. These calculations have been made for iron, nickel and magnetite. The results are given in Table V., which is taken from Kunz's[1] article.

TABLE V.

Substance.	I at 20° C.	I_m	Θ	N	$NI = H_m$	$M \times 10^{20}$
Fe	1,860	2,120	756° C.	3,850	6,560,000	5.15
Fe_3O_4	430	490	536° C.?	33,200	14,300,000	2.02
Ni	500	570	376° C.	12,700	6,350,000	3.65

In order to make similar deductions for cobalt from the experimental data, the method of calculating these quantities will be indicated. In the neighborhood of the point at which spontaneous ferromagnetism disappears, we have both the external field, H_e, and the internal molecular field, H_m, acting. That is

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[1] PHYS. REV., 30, pp. 359–370, 1910.

$$a = \frac{MH}{RT} = \frac{M(H_e + H_m)}{RT},$$
$$= \frac{M(H_e + NI)}{RT},$$

or

$$T = \frac{M(H_e + NI)}{aR}. \tag{5}$$

While the body is ferromagnetic we have

$$a = \frac{MH}{RT} = \frac{MNI}{RT}. \tag{6}$$

For values of a less than 0.7, the curve for

$$\frac{I}{I_m} = \frac{\cosh a}{\sinh a} - \frac{1}{a}$$

is a straight line, and we may take

$$\frac{I}{I_m} = \frac{a}{3}$$

and

$$I = \frac{a}{3} I_m. \tag{7}$$

This condition will certainly hold for $T = \Theta$. Hence, putting $T = \Theta$ in (6) we have

$$a = \frac{MNI}{R\Theta},$$
$$= \frac{MNI_m a}{3R\Theta}.$$

Hence

$$\Theta = \frac{MNI_m}{3R}. \tag{8}$$

Dividing (5) by (8) we have

$$\frac{T}{\Theta} = \frac{3H_e}{aNI_m} + \frac{3}{a}\frac{I}{I_m},$$
$$= \frac{3H_e}{aNI_m} + 1,$$

or

$$\frac{T - \Theta}{\Theta} = \frac{H_e}{NI},$$

by (7). Hence

$$(T - \Theta)I = \frac{H_e}{N}\Theta. \tag{9}$$

Equation (9) represents an hyperbola. The curves giving I as a function of T for iron show this between 756° C. and 920° C.

To calculate H_m, the value of N is necessary. This may be determined from (9) by taking corresponding values of I and H_e at some temperature above Θ. Solving (9) for N we have

$$N = \frac{H_e}{I}\frac{\Theta}{T - \Theta},$$

$$= \frac{1}{k}\frac{\Theta}{T - \Theta}. \tag{10}$$

N may also be calculated from a knowledge of Curie's constant, C. By Curie's Law we have

$$C = \chi T = \frac{k}{d}T,$$

where χ is the specific susceptibility, and d is the density. But

$$k = \frac{I}{H} = \frac{I}{H_e + NI}.$$

At $T = \Theta$, H_e is negligible in comparison with N. Hence for this temperature

$$k = \frac{1}{N},$$

or

$$C = \frac{1}{N \cdot d}\Theta,$$

or

$$N = \frac{d \cdot C}{\Theta}. \tag{11}$$

Having N we can calculate H_m, taking $I = I_m$, giving

$$H_m = NI_m.$$

From (8) we may obtain M, the moment of the elementary magnet, *viz.*,

$$M = \frac{3R\Theta}{NI_m} = \frac{3R\Theta}{H_m}. \tag{12}$$

Furthermore we may calculate the number of atoms which make up an elementary magnet. Let N' be the number of molecular magnets per cubic centimeter. Then

$$N'M = I_m$$

or

$$N' = \frac{I_m}{M}. \qquad (13)$$

If there are n atoms per elementary magnet and each atom has a mass of m grams, then

$$nN'm = \text{mass per unit volume} = d.$$

But

$$m = Am_H,$$

where A is the atomic weight of the substance and m_H is the mass of the hydrogen atom. Hence we have

$$n = \frac{d}{N'm} = \frac{d}{AN'm_H}. \qquad (14)$$

APPLICATION OF THEORY TO EXPERIMENTAL RESULTS.

Curve A of Fig. 7, showing σ as a function of the temperature, indicates that the Curie point is in the neighborhood of 1075° C. or 1348° Abs. From this value a theoretical curve giving σ as a function of T can be calculated as follows. The curve OA in Fig. 9 gives us the relation between I/I_m, equal to σ/σ_m, and the parameter a, and Table VI gives the values of σ/σ_m, calculated from equation (3) for various values of a. Hence if we can determine the value of T corresponding to a given value of a, we can at once determine the corresponding value of σ/σ_m either from Table VI or graphically from the curve of Fig. 9. Knowing σ_m we can then calculate the value of σ for the given value of T.

This relation between T and a comes from equation (4) which may be written in the form

$$\frac{I}{I_m} = \frac{\sigma}{\sigma_m} = \frac{R}{MNI_m}aT.$$

From equation (8) we have

$$\Theta = \frac{MNI_m}{3R}.$$

Hence

$$\frac{\sigma}{\sigma_m} = \frac{1}{3\Theta}aT,$$

and

$$T = \frac{3\Theta}{a}\frac{\sigma}{\sigma_m}.$$

This gives us the required equation, and the values of σ/σ_m are given in Table VI.

TABLE VI.

a	$\frac{\cosh a}{\sinh a}$	$\frac{1}{a}$	$\frac{\sigma}{\sigma_m} = \frac{\cosh a}{\sinh a} - \frac{1}{a}$
0.01	100.0000	100.0000	0.0000
0.1	10.0299	10.0000	0.0299
0.2	5.0676	5.0000	0.0676
0.3	3.4328	3.3333	0.0995
0.4	2.6317	2.5000	0.1317
0.5	2.1639	2.0000	0.1639
0.6	1.8619	1.6667	0.1952
0.7	1.6546	1.4286	0.2260
0.8	1.5059	1.2500	0.2559
0.9	1.3961	1.1111	0.2850
1.0	1.3131	1.0000	0.3131
1.2	1.1995	0.8333	0.3662
1.4	1.1295	0.7143	0.4152
1.6	1.0849	0.6250	0.4599
1.8	1.0561	0.5556	0.5005
2.0	1.0373	0.5000	0.5373
3.0	1.0049	0.3333	0.6716
4.0	1.0007	0.2500	0.7507
5.0	1.0000	0.2000	0.8000
6.0	1.0000	0.1667	0.8333
7.0	1.0000	0.1429	0.8571
8.0	1.0000	0.1250	0.8750
9.0	1.0000	0.1111	0.8889
10.0	1.0000	0.1000	0.9000
12.5	1.0000	0.0800	0.9200

As noted above, the work of Weiss and Onnes shows that the value of σ at the temperature of liquid hydrogen is less than 163.6. Assuming this value for σ_m, the values of σ and T corresponding to various values of the parameter a can be calculated. Thus, for $a = 0.5$

$$\frac{\sigma}{\sigma_m} = 0.1639,$$

from Table VI. Hence

$$\sigma = 0.1639 \times 163.6 = 26.8$$

and

$$T = \frac{3 \times (1{,}075 + 273)}{0.5} \times 0.1639 = 1326^\circ \text{ Abs.} = 1053^\circ \text{ C.}$$

Carrying out similar calculations for other values of a the results given in Table VII. are obtained. In this table, t is the centigrade temperature corresponding to the absolute temperature T.

TABLE VII.

a	σ/σ_m	T	σ	t
0.5	0.1639	1326°	26.8	1053°
0.7	0.2260	1306°	37.0	1033°
1.0	0.3131	1266°	51.2	993°
2.0	0.5373	1086°	87.9	813°
3.0	0.6716	905°	109.9	632°
4.0	0.7507	759°	122.8	486°
5.0	0.8000	647°	130.9	374°
6.0	0.8333	562°	136.3	289°
7.0	0.8571	495°	140.2	222°
8.0	0.8750	442°	143.2	169°
9.0	0.8889	399°	145.4	126°
10.0	0.9000	364°	147.2	91°
12.5	0.9200	298°	150.5	25°

The values of σ and t from Table VII. are plotted in curve B of Fig. 7. This curve is of the same general shape as the experimental curve, A, but it lies entirely below A. The difference between the two curves is about 10 at 0° C. and increases gradually to 20 at 600° C. From this point on up to 1050° C. the difference between the two curves at any temperature is practically constant, lying between 20 and 21. Hence if the theoretical curve is shifted up 20 divisions it will coincide with the experimental curve in the interval 500° C. to 1050° C. This is shown by the double circles in Fig. 7.

In the interval above 1070° C. the experimental curve has the general form of the hyperbola. This agrees with the requirements of equation (9).

From the data at 1104° C. we can calculate the molecular field and the moment of the elementary magnet. For this temperature we have

$$T = 1104° + 273° = 1377° \text{ Abs.}$$
$$I_m = 163.6 \times 8.77 = 1{,}435.$$

H_e	I	I/H_e
1,400	11.1	0.00793
2,400	16.6	0.00692
3,050	23.3	0.00764

Mean value of $I/H_e = k = 0.00753$.

Substituting these values in equation (10) we have

$$N = \frac{1}{0.00753} \times \frac{1{,}348}{1{,}377 - 1{,}348} = 6{,}180.$$

Hence

$$H_m = NI_m = 6{,}180 \times 1{,}435 = 8{,}870{,}000.$$

From equation (12) we have

$$M = \frac{3R\Theta}{NI_m}.$$

The value of R to be used is that corresponding to one molecule, *viz.*, $R = 1.36 \times 10^{-16}$. Hence

$$M = \frac{3 \times 1.36 \times 10^{-16} \times 1{,}348}{6{,}180 \times 1{,}435} = 6.21 \times 10^{-20}.$$

The number of elementary magnets per cubic centimeter from equation (13) is

$$N' = \frac{I_m}{M} = \frac{1{,}435}{6.36 \times 10^{-20}} = 2.31 \times 10^{22}.$$

The number of atoms making up an elementary magnet is given by equation (14), *viz.*,

$$n = \frac{d}{N'm} = \frac{d}{N'Am_H}.$$

The values to be substituted are:

$$d = 8.77, \qquad N' = 2.31 \times 10^{22},$$
$$A = 59.00, \qquad m_H = 1.61 \times 10^{-24},$$

giving

$$n = \frac{8.77}{59.00 \times 2.31 \times 10^{22} \times 1.61 \times 10^{-24}} = 4.01.$$

Hence four atoms of cobalt make up the elementary magnet. The value 4.01 is far more nearly an exact integer than the accuracy of the data would lead us to expect, and this is strong evidence of the accuracy of the value of Θ.

It is interesting to compare these results with those given in Table V. The results are summarized in Table VIII.

TABLE VIII.

	I at 20° C.	I_m	Θ	N	$NI_m = H_m$	$M \times 10^{20}$	n	N'
Fe	1,860	2,120	756° C.	3,850	6,560,000	5.15	2	4.12×10^{22}
Ni	500	570	376° C.	12,700	6,350,000	3.65	6	1.56×10^{22}
Co	1,421	1,435	1,075° C.	6,180	8,870,000	6.21	4	2.31×10^{22}

As was to be expected, the values of I and I_m for cobalt lie between the corresponding values for iron and nickel. The same is true of N and N'.

Θ however is much higher, while the intrinsic molecular field is one third larger than that of iron or nickel, and the moment of the elementary magnet is one fifth larger than that of iron and two thirds larger than that of nickel.

It is very interesting to note that the elementary magnet of cobalt consists of four atoms while the elementary magnet of iron, as indicated by the work of Kunz, consists of two atoms and that of nickel of six atoms.

Using the laws of electrolysis, another important physical constant can be calculated, namely the elementary charge, e. This is done as follows. The number of atoms per cubic centimeter of cobalt is

$$\bar{N}' = nN'.$$

Hence the number of atoms per gram is

$$\bar{N} = \bar{N}'/d = nN'/d$$

and the number of atoms per gram atom is

$$A\bar{N} = nN'A/d.$$

Hence the quantity of electricity required to deposit one gram atom is

$$Q = \frac{nN'A}{d} \cdot v \cdot e,$$

where v is the valency. But from the laws of electrolysis

$$\begin{aligned} Q &= v \cdot 96{,}540 \text{ coulombs} \\ &= v \cdot 9.65 \times 10^3 \text{ c.g.s. electromagnetic units.} \end{aligned}$$

Hence

$$\frac{nN'A}{d} \cdot v \cdot e = v \cdot 9.65 \times 10^3$$

or

$$e = \frac{9.65 \times 10^3 \times d}{nN'A}.$$

Substituting the values obtained above this gives

$$\begin{aligned} e &= \frac{9.65 \times 10^3 \times 8.77}{4 \times 2.31 \times 10^{22} \times 59} \\ &= 1.55 \times 10^{-20} \text{ c.g.s. electromagnetic units,} \\ &= 4.65 \times 10^{-10} \text{ c.g.s. electrostatic units.} \end{aligned}$$

Until the recent work of Millikan[1] the accepted value for e was 4.65 ×

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[1] Phys. Rev., 32, pp. 349–397, 1911.

10^{-10} c.g.s. electrostatic units. This exact agreement is certainly far better than would reasonably be expected, and is further evidence of the reliability of the results at high temperatures.

The recent work of Weiss mentioned above gives values for χ for the interval from 1156° C. to 1302° C. Calculations of N, M, H_m, and n based upon his results are in fair agreement with the results deduced above.

SUMMARY.

The chief results of this investigation are the following:

1. The saturation value of the intensity of magnetization of cobalt has been determined at intervals of one hundred to one hundred and fifty degrees throughout the interval from 22° C. to 1150° C.

2. The "Curie Point," or point of magnetic transformation from the ferromagnetic to the paramagnetic state, has been established at 1075° C.

3. The curve giving σ as a function of the temperature has been shown to be of the same general character as that demanded by theory, though differing from the theoretical curve by a constant amount throughout most of its length

4. The values of the intrinsic molecular field, H_m, the moment of the elementary magnet, M, the number of atoms in an elementary magnet, n, and the elementary charge, e, have been calculated and found to have the following values:

$$H_m = 8{,}870{,}000, \qquad n = 4,$$
$$M = 6.21 \times 10^{-20}, \qquad e = 4.65 \times 10^{-10} \text{ E.S.}$$

The author takes pleasure in acknowledging his indebtedness to Professor A. P. Carman for the facilities for this investigation, and to Professor Jakob Kunz both for his general supervision of the work and for many valuable suggestions.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
May 8, 1911.

THE TRANSVERSE THERMOMAGNETIC EFFECT IN NICKEL AND COBALT.

By Alpheus W. Smith.

IN an earlier paper the author[1] has studied the Hall effect in iron, nickel and cobalt at a number of temperatures between – 190° and 1100° C. For a given magnetic field the Hall effect in these metals was found to increase more and more rapidly, until the critical temperature of the metal in question was reached, where for a small additional increase in temperature the effect sinks suddenly to a small fraction of its value at that temperature and then continues to decrease with further rise of temperature. In each of these metals it is known that there is a molecular change at the critical temperature. The nickel changes from α-nickel to β-nickel; the iron from α-iron to β-iron and then to γ-iron; and the cobalt from α-cobalt to β-cobalt. These molecular transformations manifest themselves also in a change of the electrical resistance,[2] in a change of the thermoelectric heights[3] and in a change in the magnitude of the Peltier effect.[4] These latter changes are, however, not large in comparison with the change in the Hall effect or with the change in the permeability. This behavior of the Hall effect at the critical temperature allies it more closely to the magnetic properties of the metal than to either the resistance or the thermoelectric heights. It seemed of interest to examine some of the other effects which are allied to the Hall effect, in order to see in what way they are influenced by changes of temperature and by the molecular transformations which are known to take place when the metals pass from the magnetic to the non-magnetic state.

For a clear statement of the various phenomena which arise when a metal plate which is carrying either a current of heat or a current of electricity is brought into a magnetic field so that the lines of force are normal to the plane of the plate, reference is made to the paper by H. Zahn[5] and to the paper by Hall and Campbell[6] on these phenomena. For our present purposes it is only necessary to recall that when a metal

[1] Phys. Rev., 30, p. 1, 1910.

[2] Harrison, Phil. Mag. (6), 3, p. 183.

[3] Ibid., p. 192.

[4] Cermak, Ann. der Phys., 24, p. 351, 1907.

[5] Ann. d. Phys., 14, p. 886, 1904.

[6] Proc. Amer. Soc. of Arts and Sci., 46, p. 625, 1911.

plate which is carrying a longitudinal electrical current is brought into a magnetic field so that the lines of force are perpendicular to the plane of the plate, there is set up in the plate a transverse electromotive force whose magnitude is given by the equation,

$$E = R\frac{Hi}{d},$$

where E is the electromotive force in absolute units; H, the magnetic field in absolute units; i, the current in absolute units; d, the thickness of the plate in centimeters.

When a similar plate through which there is a longitudinal flow of heat is brought into a magnetic field in the way indicated above there is set up by the magnetic field a transverse electromotive force given by the equation,

$$E = Q\beta H\frac{\partial T}{\partial x},$$

where E is the electromotive force in absolute units; β, the width of the plate in centimeters; H, the magnetic field in absolute units; $\partial T/\partial x$, the temperature gradient in the plate in degrees Centigrade per centimeter; Q, a constant which is a function of the temperature of the plate and sometimes of the magnetic field. This phenomenon is known as the transverse thermomagnetic effect or as the Nernst effect. Its variation with the temperature of the plate and its relation to the Hall effect and to the magnetic properties form the subject of the present paper.

Apparatus and Method.

For the study of the transverse thermomagnetic effect between room temperature and 100° C., the apparatus for securing the desired temperature gradient in the plates, was the same as that used by the author[1] in the study of this effect in alloys. It consisted essentially of two copper tubes to each of which was soldered a narrow strip of copper about 0.5 cm. in thickness. To these copper strips were soldered the ends of the plates to be investigated. Through one of the tubes flowed steam at atmospheric pressure; through the other tube, water at room temperature. The plates which were about 4 cm. long, 1.5 cm. wide and 0.1 cm. thick, were cut from a larger sheet of the metal so that narrow arms projecting from the middle of each of the longer edges, extended some distance out of the magnetic field. To the ends of these arms which were filed down until they were about 0.1 cm. in diameter were soldered the copper lead wires which lead to the galvanometer on which the effect was to be observed. Where the original sheet was not large enough to allow arms of sufficient length to extend out of the magnetic field, the arms were built up out of shorter pieces of the metal by silver-soldering these pieces together. By means of these arms the error due to the transverse galvanomagnetic effect discovered by Leduc[1] is eliminated, for the junction of the lead wire and the plate can not form a thermal couple since both are of the same material. To determine the temperature gradient in the plate a copper-nickel thermal couple was soldered to either end of the plate on a line midway between its upper and lower edges.

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[1] Phys. Rev., 32, p. 178, 1911.

To secure the desired temperature gradients in the plate at temperatures above 100° C. an electric heating device was constructed. It consisted essentially of two copper rods *A* and *B* (Fig. 1*a*). These rods were about 3.5 cm. in diameter and about 13 cm. in length. They were connected by the brass bar *LM* in such a way that they were electrically insulated from each other. Around each of these rods was wrapped two layers of nichrome wire, insulated from each other and from the rods by means of asbestos and strips of mica. The rods and their windings were then covered with a large number of layers of asbestos paper to afford protection against the loss of heat. The coils of nichrome wire were then connected independently to a suitable source of alternating current. By sending suitable currents through these coils any desired temperature gradient could be obtained and the temperature of the plate could be increased or decreased at will. In order to fasten the ends of

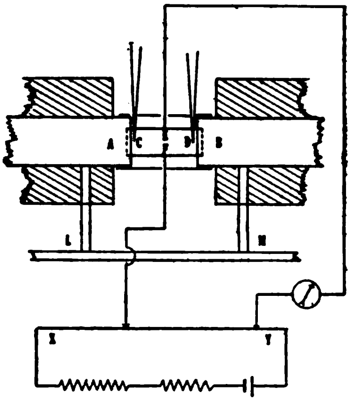

Fig. 1a.

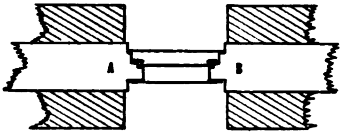

Fig. 1b.

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[1] Compt. Rend. 104, p. 1785 (1887).

the plates to the ends of the rods, the rods were cut away as indicated in Fig. 1*b* which is a cross section of the rods and plate perpendicular to the plane of the plate. The plate was held in the recess provided for it by means of heavy copper clamps which fastened it firmly to the copper rod. To prevent the lateral flow of heat from the plate and to insure as far as possible a uniform temperature gradient in the plate, it was enclosed in a thin box of non-conducting material. The front and back of the box (Fig. 1*b*) were made of thick sheets of mica which were fastened by means of screws to the ends of the copper rods. The top and bottom of the box were made of heavy asbestos board, also fastened by screws to the ends of the copper rods. This box was about 1.8 cm. thick, 4 cm. high, and about 5.5 cm. long. It was filled with powdered magnesium oxide and when the plate was in position there was between the plate and the walls of the box an insulating layer of this magnesium oxide about 0.8 cm. in thickness.

At *C* and *D* (Fig. 1*a*) was clamped a thermal couple to determine the temperature gradient in the plate. For the lower temperatures copper-nickel thermal couples were used; for higher temperatures, platinum-platinum-iridium couples. From *E* and *F* projected the arms which were cut out of the larger sheet of metal in the manner already described. To these arms were soldered the lead wires which after protection against thermal electromotive forces lead through the galvanometer to the potentiometer *XY* on which the difference of potential between *E* and *F* was measured in the usual way. There was also in the circuit with the galvanometer an auxiliary potentiometer for compensating the thermal electromotive forces that happened to be in the circuit.

The cobalt and the nickel for one of the nickel plates was obtained from Kahlbaum. The nickel for the other nickel plate was furnished by Eimer and Amend and referred to by them as chemically pure.

The plate was placed between the poles of the magnet in the usual manner and rigidly supported. The currents in the heating coils were then regulated until the desired temperature gradient was secured. When the thermal couples showed that temperature equilibrium had been established, the thermal electromotive forces which happened to be in the galvanometer circuit were as nearly as possible compensated and the difference of potential produced between the edges of the plate by the establishment of the magnetic field was then measured. The direction of the magnetic field having been reversed, the corresponding difference of potential was again measured. The mean of these two observations was taken as the electromotive force called forth by the magnetic field. Sometimes the differences of potential obtained for opposite directions of the magnetic field were not equal, because there was some change in the thermal electromotive forces in the reversal of the magnetic field. It was found, however, that the mean of the observations just described eliminated this dissymmetry. These observations were repeated a number of times for each magnetic field and the mean of these observations has been used in the subsequent figures and tables. The magnetic fields were measured ballistically by comparison with a standard solenoid. For the greater part of the work the temperature gradient in the plate was about 25° C. per centimeter, but in a few cases it had to be somewhat greater or less than 25° C. per centimeter. The mean of the temperatures of the ends of the plate was taken as the temperature of the middle of the plate where the difference of potential was observed.

Results.

The results of these observations on the nickel plate from Eimer and Amend have been plotted in Fig. 2 and those on the plate of Kahlbaum nickel in Fig. 3. The abscissæ in these figures are the magnetic fields in absolute units and ordinates are the corresponding differences of potential reduced to the case of a plate which is 1 cm. wide and has a temperature gradient of 1° C. per cm. in it. From an examination of these figures it is seen that at the lower temperatures the electromotive force is at first proportional to the magnetic field, until the field reaches a value of about 5,000 absolute units. Above such fields a large increase in the magnetic field is accompanied by only small increases in the corresponding difference of potential. With this increase of the magnetic field the Nernst electromotive force seems to approach a limiting value just as the intensity of magnetization approaches a limiting value with an increase of the magnetizing force. As the temperature is increased the fields at which proportionality between the magnetic field and the Nernst electromotive force ceases, become smaller, so that the bends in the curves in Figs. 2 and 3 shift toward the left. It will be noticed from these curves that the fields for this saturated condition are somewhat larger for the plate of Eimer and Amend nickel than for the plate of Kahlbaum nickel. For the same temperature and equal magnetic fields the Nernst electromotive force is in general greater in the nickel plate from Eimer and Amend than in the nickel plate from Kahlbaum. When a temperature of about 350° C. has been reached, the electromotive force for low fields is still increasing with rise of temperature but the electromotive force for high fields where the saturated condition is being reached is less than the corresponding electromotive force for a temperature of about 300° C. At about 370° C. for the plate of nickel from Eimer and

Amend and at about 380° C. for the plate of Kahlbaum nickel the character of the curve relating the Nernst electromotive force and the magnetic field has completely changed. There is still evidence of an approach to the saturated condition but it is not possible to reach that condition with the fields available in these experiments. Above 400° C. the nickel has lost its magnetic properties and the Nernst electromotive force seems to be proportional to the magnetic fields over the range of fields used in these experiments. The magnitude of the effect decreases rapidly for small increases of temperature above the critical temperature, so that at about 400° C. for a magnetic field of about 2,500 absolute units the Nernst electromotive force is only about one twentieth of the corresponding electromotiev force at a temperatur slightly less than the criteical temperature.

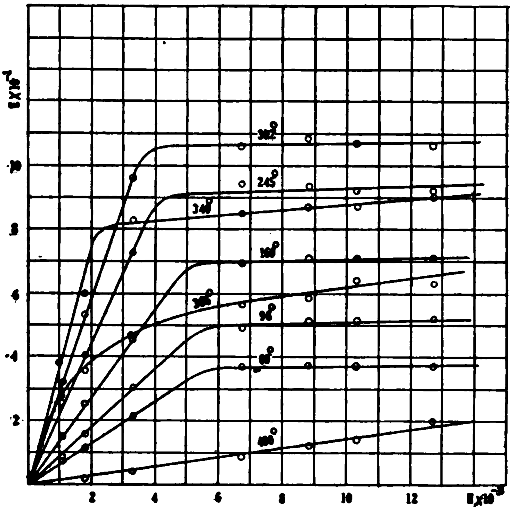

Fig. 2.
Nickel from Eimer and Amend.

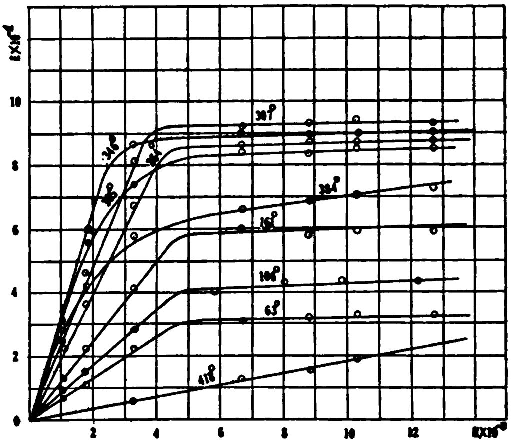

Fig. 3.
Kahlbaum Nickel.

The curves given in Figs. 2 and 3 are very similar in character to the corresponding curves relating the Hall electromotive force and the magnetic field. The reason for the shift in the bends in these curves toward lower fields is the same as the reason assigned for the corresponding shift in the bends in the curves for the Hall effect. Both the Hall electromotive force and the Nernst electromotive force seem to be proportional to the intensity of magnetization in the plate rather than to the magnetic field, so that when the intensity of magnetization has reached its maximum value the Hall electromotive force and the Nernst electromotive force will reach a maximum value. In nickel the maximum value of the intensity of magnetization decreases continuously with the rise of temperature, at first slowly and then more more rapidly, as the critical temperature is approached. Hence the higher the temperature the lower the field in the air-gap necessary to produce saturation in the plate.

In Fig. 4 the value of Q in the equation $E = Q\beta H\partial T/\partial x$ has been plotted against the absolute temperature of the plate. The values are

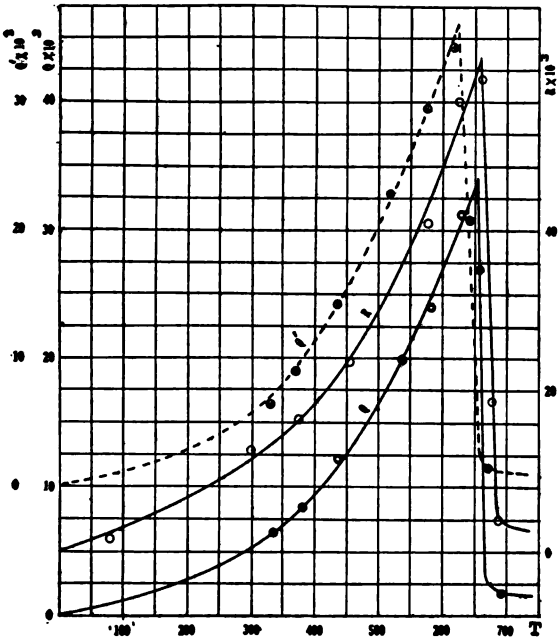

Fig. 4.

Nickel.

plotted for the region where the preceding curves showed that there was a proportionality between the Nernst electromotive force and the magnetic field. The lower curve is for the plate of Kahlbaum nickel; the upper curve for the plate of nickel from Eimer and Amend; the middle curve is taken from the previous paper and shows the relation between the Hall constant R and the absolute temperature. The ordinates on the right refer to the Hall effect; those on the left to the Nernst effect. Q means the constant for the Kahlbaum nickel plate and Q' the constant for the plate of Eimer and Amend nickel. The curves have been displaced vertically in order to avoid superposition. It is seen that the character of the curve is the same whether it is for the Hall effect or for the Nernst effect. The sudden decrease in the Hall effect and the corresponding decrease in the Nernst effect occur at nearly the same temperature. The curve for Q as well as that for Q' has been extended back to the absolute zero.

Table I. contains the values of Q, Q' and R read off of the curves in Fig. 4 at intervals of fifty degrees between 300° and 650° absolute. In the last column of this table the ratio of Q to R has been tabulated, and in Fig. 7 this ratio is plotted against the absolute temperature. From this ratio it is seen that Q increases more rapidly than R with increase of temperature. The comparison between the values of Q' and R is less certain because the plate in which Q' was determined and that in which R was determined certainly differed somewhat in purity. The results on the nickel plate from Eimer and Amend, however, confirm the results on the Kahlbaum nickel plate. At 32° C. the value of the Nernst effect is nearly the same in the two plates. With rising temperature it increases somewhat more rapidly in the Eimer and Amend plate than in the Kahlbaum plate, but at their respective critical temperatures the magnitude of the effect in both plates is about the same. The critical temperature in the former is reached earlier than in the latter. As the critical temperature is approached the ratio of Q to R approaches a constant value. Nernst[1] found Q to have a value of 8.01×10^{-3} at 56° C. when the magnetic field was about 830. At about the same temperature Zahn[2] gives for one plate of nickel $Q = 1.3 \times 10^{-3}$ when the magnetic field is 10,620; for another plate of nickel he gives for $Q = 3.55 \times 10^{-3}$ when the magnetic field is 6,290. The value given in this paper is larger than the value given by Zahn and less than that given by Nernst. This lack of agreement between the values obtained by different observers may be attributed to impurities in the nickel.

TABLE I.

Nickel.

Abs. Temp.	$R \times 10^3$	$Q \times 10^3$	$Q' \times 10^3$	$Q/R \times 10$
300°	11.2	5.25	5.25	4.69
350	14.8	7.25	7.7	4.90
400	18.8	9.75	11.3	5.19
450	24.0	13.0	16.0	5.42
500	30.2	16.7	21.2	5.53
550	37.6	21.3	26.2	5.67
600	46.8	27.0	32.5	5.77
650	59.0	34.0	—	5.76

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[1] W. A., 31, p. 760, 1887.

[2] Ibid., p. 921.

Fig. 5 shows the relation between the Nernst electromotive force in cobalt and the magnetic field. The electromotive force is approximately proportional to the magnetic field over the range of fields used in these experiments. At 56° C. there is a suggestion that the saturated condition is being reached but at higher temperatures it is not possible to reach saturation with the magnetic fields here available. In the work on the Hall effect it was seen that between − 190° C. anda bout 300° C. the fields necessary to obtain saturation increased with rising temperature and for higher temperatures there is a corresponding decrease with rising temperature. The field for which saturation begins to appear at 56° C. in the Nernst effect seems to be nearly equal to the field at which saturation begins to appear in the Hall effect at the same temperature. The shift toward higher fields agrees with the corresponding shift in the Hall effect. The explanation of this shift is the same as that given for the analogous shift in nickel.

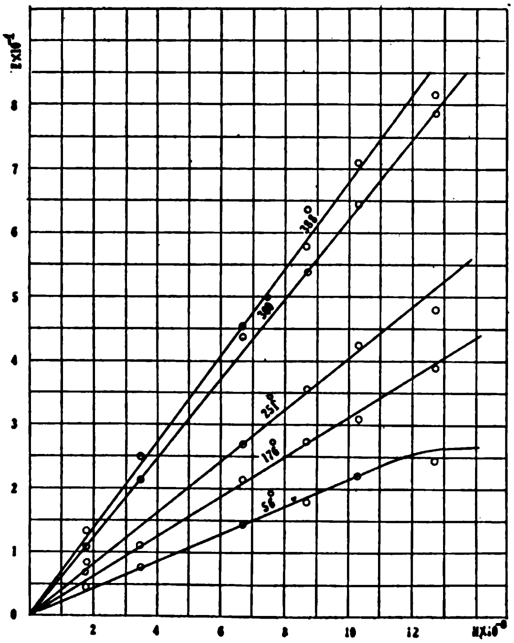

Fig. 5.

Cobalt.

The curves in Fig. 6 show the relation between Q and the temperature and the relation between R and the temperature in cobalt. The abscissæ are temperatures on the absolute scale; the ordinates on the right are for R and those on the left are for Q. The character of the two curves is essentially the same but R increases a little more rapidly than Q, so that the ratio of Q/R decreases with rising temperature. This decrease becomes less rapid at higher temperatures and apparently the ratio approaches a constant value. The values of Q and of R have been read off of these curves at intervals of fifty degrees and the values tabulated in Table II. The last column of that table contains the ratio Q/R. In Fig. 7 this ratio has been plotted against the absolute temperature. Zahn gives for the value of Q in cobalt 1.8×10^{-8}; Nernst found for it the value 2.24×10^{-8}. The value 1.80×10^{-8} for the plate studied in this paper agrees well with the value given by Zahn.

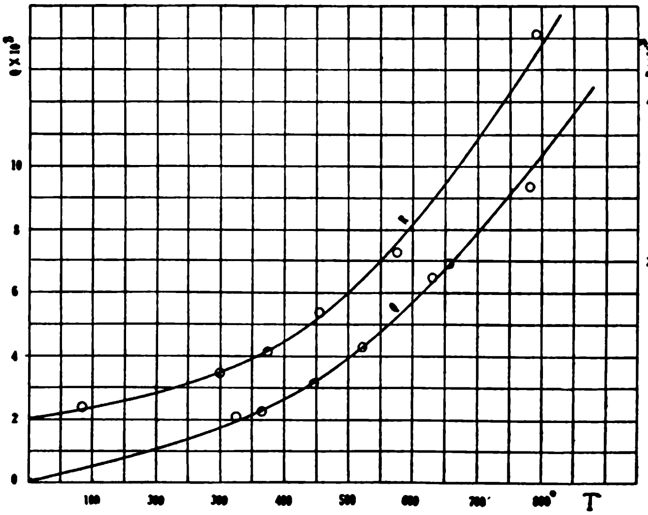

Fig. 6.
Cobalt.

In Fig. 7 besides the curves showing the relation in nickel and cobalt between Q/R and the temperature a similar curve has been plotted for soft iron from the data of Hall and Campbell.[1] In nickel the least magnetic of these substances Q increases more rapidly than R; in cobalt which is more magnetic than nickel but less mangetic than iron Q in-

Table II.

Cobalt.

Abs. Temp.	$R \times 10^8$	$Q \times 10^8$	$Q/R \times 10$
300°	5.88	1.80	3.00
350	7.60	2.15	2.83
400	10.0	2.70	2.70
450	12.6	3.30	2.62
500	16.0	4.00	2.50
550	20.0	4.85	2.42
600	24.6	5.70	2.32
650	29.6	6.75	2.28
700	35.0	7.80	2.23
750	40.8	8.90	2.18
800	46.8	10.00	2.16

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[1] Ibid., p. 644.

creases somewhat less rapidly than R; and in iron Q increases much less rapidly than R. It seems that the more magnetic the substance the more rapid will be the decrease of Q/R with rising temperature and that for a metal no more magnetic than nickel this ratio will increase.

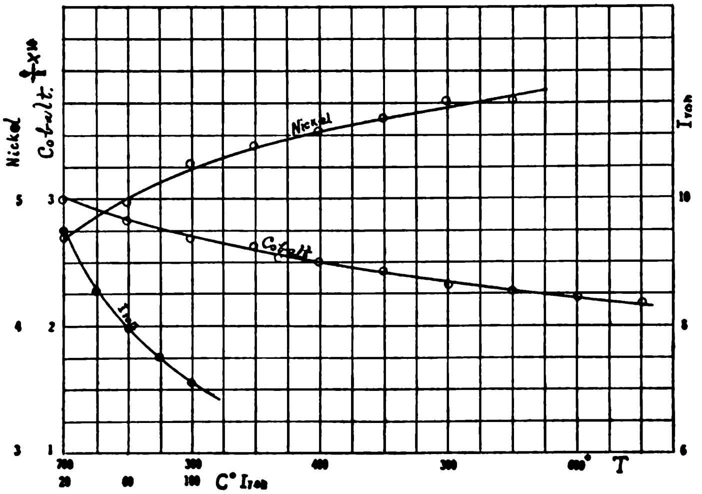

Fig. 7.

The behavior of the Hall effect and the Nernst effect where the molecular transformation from α-nickel to β-nickel takes place is of interest in connection with the relation between these effects and the resistance and the thermoelectric heights of the metals. Baedeker[1] has called attention to the fact that an increase of resistance is accompanied by an increase in the Hall effect. The author's[2] observations on the Hall effect in alloys points to the same conclusion, but they also make evident that there is not a proportionality between the Hall effect and the resistance in alloys. The data here given together with the data by Harrison[3] on the resistance of nickel shows that the resistance depends on the temperature in a different way from the way in which the Hall effect and the Nernst effect depend upon it. At the critical temperature there is a small decrease in the rate at which the resistance increases with the temperature but there is a marked decrease in the Hall effect and in the Nernst effect. The factors which determine the changes in the former can only determine to a small degree the changes in the latter. A relation between the thermoelectric heights and the Hall effect has been previously pointed out. The metals which have the largest thermoelectric height with respect to lead have in general the larger Hall effects. The observations of Harrison on the thermoelectric heights of nickel and those of Cernak[1] on the Peltier effect in nickel show in each of these phenomena only small changes at the critical temperature. Neither the Hall effect nor the Nernst effect can be therefore regarded as determined completely by the factors which determine the thermoelectric heights and the Peltier effect.

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[1] Electr. Erscheinungen in Metallischen Leitern, p. 104.

[2] Phys. Rev., 32, p. 178, 1911.

[3] Phil. Mag. (6), 3, p. 177.

Summary.

The chief results of this paper are:

1. The relation between the Nernst electromotive force and the magnetic field has been examined in nickel at a number of temperatures between 56° and 410° C. For a given magnetic field it has been found to increase with rising temperature until the critical temperature has been reached. The rate of increase becomes greater the nearer the critical temperature is approached. In passing the critical temperature the Nernst effect sinks to a small fraction of its value at that temperature and then probably decreases with further rise of temperature.

2. For any particular temperature below the critical temperature the Nernst electromotive force is at first proportional to the magnetic field but when the intensity of magnetization approaches its maximum there is a rapid deviation from this proportionality and the electromotive force approaches a limiting value at higher magnetic fields. Since the maximum intensity of magnetization decreases with rising temperature, the fields necessary to produce saturation become less as the temperature is increased.

3. At temperatures above the critical temperature the Nernst electromotive force is proportional to the magnetic field.

4. The study of the Nernst effect in cobalt between 56° and 550° has showed that the Nernst electromotive force is proportional to the magnetic field over that interval of temperature and over the range of magnetic fields in these experiments.

5. In nickel the Nernst effect increases more rapidly than the Hall effect with rising temperature and in cobalt it increases less rapidly than the Hall effect. In this respect cobalt behaves like iron.

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[1] Ann. der Phys., 24, p. 351, 1907.

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THE DISTILLATION OF AMALGAMS AND THE PURIFICATION OF MERCURY.

By G. A. Hulett.

Distillation of Amalgams.

IN a previous article,[1] it was shown that measurable quantities of some of the common metals distil over with the mercury vapor when they are present with the mercury in the still. It seems that in the distillation of amalgams, just as in the case of other liquid mixtures, that a complete separation is impossible. It was found, however, that when a little air was allowed to pass over with the mercury vapor during the distillation that most metallic vapors were odixized while mercury vapor was not affected. On distilling zinc amalgams with a little air bubbling up through the mercury and passing over with the vapors, no zinc was detected in the distillate although we were able to detect one part of zinc in 10^{10} parts of mercury.[2] Zinc amalgams were also distilled in an ordinary Weinhold still where the air was all displaced by mercury vapor and the distillation was carried on in a space which was free from all gases except mercury vapor. Under these conditions it was always possible to detect zinc in the distillate, even when there was only a trace of zinc in the mercury in the still.

The above experiments suggested that all readily oxidizable metals such as zinc, cadmium, bismuth, tin, copper, lead, etc., might be effectively removed by one distillation. The simplest method of accomplishing this result was to use an ordinary distilling flask with suction and so arranged that a little air bubbled through the mercury in the still and passed over with the vapors. This arrangement, just as for other liquids, prevented the troublesome bumping and spurting of the mercury.[3] The distillation was carried out in a flask where the air pressure was about 25 mm. or about 5 mm. partial pressure of oxygen, and the temperature was about 200° C. Any metallic vapor will completely oxidize under these conditions if the dissociation pressure of its oxide is less than the partial pressure of the oxygen maintained in the still. This is eminently true of all the common base metals. These oxides collect on the distillate and when they are present in considerable quantity as in the case of quite impure mercury, the distillate may then look dirty but when filtered through a pinhole in a filter paper is found to be free from the metals, provided sufficient air passes over with the vapors.

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[1] Phys. Rev., 21, 288.

[2] L. c., p. 391.

[3] The bumping does not seem to take place with mercury when the air is all removed, as in the case of the Weinhold still, but is very troublesome when a little air is present except when it is bubbled through the mercury.

Mercury vapor does not seem to oxidize under the conditions given above since kilograms of pure mercury may be distilled without a suggestion of oxide appearing on the top of the "Sprengle" column (Fig. 2), while the merest trace of oxide is very noticeable. When the partial pressure of the oxygen is much more than 5 mm., mercury oxide appears. The work of Pelabon[1] indicates a very low dissociation pressure of mercury oxide at 200° C., but this is an extrapolated value and may be considerably in error. The oxides of silver, gold and the platinum metals would not form under the conditions in our still so their vapors would condense with the mercury vapor and be found as amalgams. On the other hand the vapor pressure of these metals must be very small at 200° C. as their melting points are 960° for silver, 1063° for gold and 1750° for platinum, furthermore the partial pressures of these vapors from dilute solutions in mercury would be even less than the vapor pressures of the metals themselves and it was hardly to be expected they would distill over in detectable quantities, however, it seemed well to test this conclusion experimentally.

Silver amalgams were first studied. A still, such as is described below, was charged with 6,800 grams of pure mercury and 35 grams of purest silver. It was thought that this would form a saturated solution at 200° as the solubility of silver in mercury is very small. This amalgam was distilled with a slow current of air passing through the amalgam in tiny bubbles and there was no suggestion of bumping or spurting. The fact that oxidizable metals are completely removed by one distillation in this apparatus is evidence that none of the amalgam in the still is mechanically carried over as a spray. The residue left in the still was a white sponge of silver which contained some mercury. The distillate was brought into a clean flask and distilled again, there was a small residue of silver sponge about 5 mm. in diameter left in the still together with several white spots distributed about the lower part of the still. These residues were dissolved in a little nitric acid and the solution sucked up into a little specially made pipette and then transferred to a small weighed porcelain crucible. The flask was thoroughly washed with a little water which was removed with the pipette and this washing repeated several times. The solution and washings were evaporated and glowed and then heated to the melting point of silver to expel the mercury. 12.7 milligrams of silver was recovered and as this amount distilled over with 6,775 grams of mercury it appears that the distillate contained one part of silver to 533,000 parts of mercury or not quite two parts in a million when distilled from a saturated silver amalgam. This distillate had furnished a second distillate which was redistilled and a residue amounting to .19 milligrams of silver was obtained so the second distillate contained some .03 parts of silver in a million. The third distillate left no visible residue on distillation. It would therefore appear to be necessary to distill mercury at least three times if it contains silver and it is quite impossible to entirely remove silver from mercury by chemical means or any other method. It was noticed that mercury containing these small traces of silver very readily became "dirty" when agitated and was noticeably different from pure mercury in its behavior.

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[1] C. R., 128, 825.

A gold amalgam was next distilled. 6,750 grams of mercury from the above experiment was brought into the still together with 45.5 grams of pure gold which had been electrically refined. This amalgam was distilled as above, the gold was left behind as a beautiful sponge which contained some mercury. The distillate was redistilled and left a distinct gold stain in the bottom of the still which was about 4 mm. in diameter, together with several smaller stains. These stains were dissolved in a little aqua regia, evaporated, glowed and found to weigh .18 milligrams. This gold was dissolved and determined colorimetrically by the method of T. K. Rose.[1] The color obtained was slightly less than that given by .2 mg. of gold in the same volume but the comparison was not particularly sharp. Evidently the weight obtained was reliable so the distillate from a saturated gold amalgam contains .027 part of gold to a million of mercury. The second distillate left a barely visible residue of gold which was colorimetrically determined to be very much less than .01 mg.

6,700 grams of mercury were now brought into the still together with 12.25 grams of platinum foil. This was ordinary foil which had been etched with aqua regia and then glowed. Soon after the distillation began the foil amalgamated and sank to the bottom of the still. The 12.25 grams of platinum was much more than was necessary to saturate the mercury at 200° and it was largely left behind as foil at the end of the distillation. The last of the mercury clung to the platinum foil and as it distilled the foil assumed the appearance of having been platinized. The solubility of platinum in mercury at 200° is evidently very small but the mercury was at all times saturated with platinum and must have had a partial pressure of platinum equal to the vapor pressure of platinum at the same temperature. The distillate was redistilled and left a very distinct stain of platinum which was collected as above, evaporated glowed and again dissolved in aqua regia. It was found by a colorimetric method to be .067 mg. of platinum. If a little stannous chloride is added to an acid solution of platinum a clear golden color is obtained when the platinum concentration is very small. This color is very stable and can be quite exactly duplicated with solutions containing known amounts of platinum. It appears therefore that mercury which distills from a platinum saturated amalgam at 200°, contains one part of platinum to one hundred million parts of mercury. The 6,700 grams of mercury distilled as a vapor occupied, at 200° and 25 mm. pressure, 39,540 liters and the .067 mg. of platinum in this volume would show a partial pressure of .00000026 mm., assuming that platinum, like the other metals is monatomic in the gaseous state. This figure then represents the vapor pressure of platinum at 200°, since the amalgam in the still was saturated with platinum. This is of course only to be regarded as giving the order of magnitude of this constant, but with proper precautions there seems to be no reason why a fairly reliable value for the vapor pressures of these metals might not be obtained in this way. If we take the value for the number of atoms in a cubic centimeter of a gas at standard temperature and pressure,[1] a calculation shows that with each cubic centimeter of mercury vapor which passed out of the still there were 5.3×10^9 atoms of platinum. From this then each cubic centimeter of space or gas which is in equilibrium with platinum at 200° contains some five billion atoms of platinum.

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[1] Chem. News, 66, 271.

THE PURIFICATION OF MERCURY.

Mercury is one of the indispensable things in scientific work. Some properties which render it especially useful are its density and that it is a liquid with a negligible vapor pressure while gases are insoluble in it. Mercury is acted upon chemically by but a few substances and, due to its position in the voltaic series, it may be used in contact with most salt solutions and so has played a fundamental role in the development of electrochemistry. Mercury does not oxidize readily under ordinary conditions although the dissociation pressure of mercury oxide is very small at ordinary temperatures.[2] Evidently it is a question of rate for pure mercury will remain bright in contact with air or oxygen almost indefinitely but a little ozone soon causes the mercury to tarnish, also the presence of the merest traces of metals dissolved in mercury cause it to tarnish and readily assume the form of very small globules which do not coalesce with the main mass and so the mercury acquires a "dirty appearance" and wets or sticks to glass and other substances. It is assumed that the base metal oxidizes and forms a coating about the little mercury globules but the effect may be obtained when silver, gold or platinum are dissolved in mercury. It is quite possible that the foreign metals catalyse the oxidation of the mercury. The fact is that the merest traces of foreign metals have a most remarkable effect on the physical properties of mercury and very seriously interfere with its use in scientific instruments and investigations so it is necessary to have mercury of a higher degree of purity than any other substance we work with as evidenced by the very large number of methods which have been proposed for purifying mercury.

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[1] Millikan, Phys. Rev., 32, 396.

[2] Pelabon, C. R., 128, 825.

The chemical methods depend upon the property of most metals to displace mercury from solutions. When an amalgam is brought into contact with a solution which contains mercury, the metal in the amalgam will displace mercury from the solution, but these are reversible reactions and even in the case of such electropositive metals as zinc and cadmium the removal from mercury cannot be complete and to a much less degree in the case of such metals as copper, lead and tin which are much nearer mercury in the voltaic series while there is little to be gained in the case of such metals as silver, gold and platinum by the chemical methods and acid solutions. If we treat mercury or dilute amalgams with an oxidizing acid mercury goes into solution and we have a solution containing mercury, and while some of the base metal is directly oxidized, most of it simply displaces the mercury in solution. Making mercury anode in acid or salt solutions[1] leads to the same result. In cyanide solutions mercury as anode might loose some metals more completely than in acid solutions.[2]

The well-known apparatus of L. Meyer,[3] is a most convenient and effective device for the chemical purification of mercury. The mercury flows in a thin stream through a long column of dilute nitric acid, or better a nitric acid solution of mercurous nitrate and is delivered bright and dry. This apparatus was noticeably improved by J. H. Hildebrand,[4] by a modification which allows the mercury to flow faster and still to divide into much finer globules. If an outlet tube with a glass cock is sealed into the lower part of the bend in the "goose neck" the last of the mercury and the solution may be run out separately and the apparatus may be easily cleaned even when it is fastened in a permanent position. Mercury left in contact with nitric acid or mercurous nitrate solution slowly forms basic salts which are insoluble and troublesome.

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[1] Jaeger., Wied. Ann. 48, 209, 1893.

[2] Battel, Chem. News, 97, 158.

[3] Zeit. anal. Chem., 2, 241.

[4] J. Amer. Chem. Soc., 31, 933 and C. J. Moore. Jour Amer. Chem. Soc., 32, 971.

The method proposed by Crafts[1] of drawing air through a long column of mercury, causes some oxidation of the base metal. It also causes a great deal of the mercury to become finely divided. We caused filtered air to bubble through a dilute cadmium amalgam (1 in 10,000) at the rate of 3 cc. per minute for four days and were able to detect cadmium in the mercury after this treatment. It is less effective than the chemical method and not as convenient.

The chemical purification of mercury is sufficient for many uses and it is a very simple and convenient operation with the V. Meyer apparatus. The chemical purification may also be effectively carried out by bringing the mercury and an acid solution of mercurous nitrate into a separatory funnel and vigorously shaking for several minutes. The mercury is then run into a second separatory funnel which contains water and from thence onto a filter with a pinhole. The chemical purification should precede the distillation so as to avoid undue clogging of the still.

The only way to effectively remove metallic impurities from mercury is by distillation and from the results given in the first part of this paper, it would seem to require two or three distillations if silver, gold or the platinum metals are present. Silver is distinctly the most difficult to remove. In the case of such metals as zinc, cadmium, lead, tin and bismuth which have a very low melting point and greater vapor pressures, it would take many distillations to satisfactorily remove these metals if the distillation was carried out in a vacuum or a reducing atmosphere. An ingenious apparatus for distilling mercury in a vacuum was devised by Weinhold[2] and modified by many other investigators. The arrangement is such that all the gases are removed by the mercury vapor and the distillation is also continuous. After the mercury vapor removes all other gases the distillation proceeds quietly and satisfactorily but we have found[3] that low melting metals like zinc distil over with the mercury and may be detected in the distillate even when there is only a trace of the metal in the mercury in the still.

We have found, however, that all oxidizable metals may be effectively removed by a single distillation if a little air is allowed to bubble through the amalgam in the still and pass over with the mercury vapor. It appears that the oxidation of the base metal occurs in the vapor phase and not to any extent while the air is bubbling through the amalgam in

[1] Bull. Soc. Chim., Paris, 49, 856.

[2] Carls, Repertorium, 9, 69.

[3] L. c., 390.

the still since the distillate from concentrated amalgams was found to be pure mercury, although the amalgam in the still contained much more base metal than could be oxidized by the small amount of air which was admitted. The following experiment was also tried: 160 c.c. of a one to ten thousand cadmium amalgam was brought into the still and was heated for four hours with air bubbling through in the usual way. The condensed mercury was allowed to flow back into the still and at the end of this time the mercury in the still had shown only a slight decrease in cadmium concentration, so it is evident that only a little of the oxygen of the air is used up in passing through the mercury in the still but in the gas phase all metallic vapors of the base metals are completely oxidized.

The question of the solubility of oxygen in mercury has been brought up by T. W. Richards and J. H. Wilson.[1] In preparing mercury for their work on amalgam concentration cells these authors used our still but employed hydrogen instead of air. This of course defeats the main advantage of this form of still. Richards and Hunt feared that the mercury distilled with air, contained dissolved oxygen but they gave no experimental evidence to support this view. The absorption of oxygen by mercury has never been detected even where the gas has been in contact with mercury at great pressures. On releasing such systems an effect should have been observed at the surface of the mercury even if the solubility was very small. Amagat[2] investigated this question and could find no evidence of absorption of oxygen at ordinary temperatures and high pressures nor any oxidation even at 100° and considerable pressures provided that the mercury and oxygen were pure. Furthermore the Weather Bureau at Washington has under observation three barometers which have been in use for over thirty years. At present they give the same readings as new barometers so there has been no deterioration of the vacuum in these barometers, and .05 mm. would have surely been detected. Now the mercury in the cisterns of these barometers soon became "saturated" with oxygen at a pressure of 150 mm. as there was contact with the atmosphere. The variations of the barometric pressure and diffusion soon brought this mercury into the barometer tube and to the top of the column where it would loose any oxygen which had been dissolved and we would expect a continually deteriorating vacuum. If the volume of the space above the mercury column is 10 c.c., .05 mm. would require only .0008 mg. of oxygen. The fact that less than this amount of oxygen got in during thirty years will give some idea of the insolubility of oxygen in mercury. The merest trace of foreign metals in the mercury starts oxidation as evidenced by a tarnish that appears on the mercury, a most delicate test, but with really pure mercury we are of the opinion that the absorption or oxidation of oxygen by mercury does not occur or that it is an infinitesimal of a higher order.

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[1] Zeit. Phys. Chem., 72, 136.

[2] C. R., 91, 812, and 93. 308.

The information gained in this and previous investigations give the essential conditions for obtaining pure mercury and it may be questioned whether any single substance may now be prepared in as high a state of purity as mercury. For small quantities of mercury a simple still may be constructed from materials found in any laboratory: Fig. 1 gives an idea of the essential details, *g* is a common "Asbestos Air Bath" with a hole in the bottom for the flame and above this there is fastened a shallow metal cup which supports the flask and on which the flame plays. The flask *a* is an ordinary round bottom flask holding from 250 to 500 c.c. The neck is drawn down short and the 20 cm. tube *b* sealed on and also the side tube *e* which is thin walled and 10 to 15 mm. in diameter and 50 cm. long, *e* serves as the air condenser. A tube *c* is selected of such a diameter that it will just nicely fit into the tube *b* and to this is sealed a glass cock while it is drawn out to a fine capillary at the lower end. This tube is slipped into the tube as indicated in the cut. The joint *d* where there is a slight enlargement of the tube *c*, is made tight with thin rubber bands which are about one centimeter wide. These bands are wrapped about the joint while stretched thus making a tight and simple joint. The asbestos shields *s*, *s* deflect the hot gases so that this joint never gets even warm to the hand. This is much simpler than a ground joint which may be used here. The glass cock regulates the rate at which the gas bubbles through the mercury in the still and if it is well ground no fat need be used on it. The end of the condensing tube *e* is sealed to the stopper of an ordinary Drexel Washing Bottle. The outlet tube from the Drexel bottle *f* is joined to an ordinary Sprengle suction pump and a manometer and a vacuum of 25 to 30 mm. maintained in the system while air is bubbling through the mercury in the still. When the still is once uniformly in operation it needs little attention and a couple of kilograms of mercury may be distilled in two or

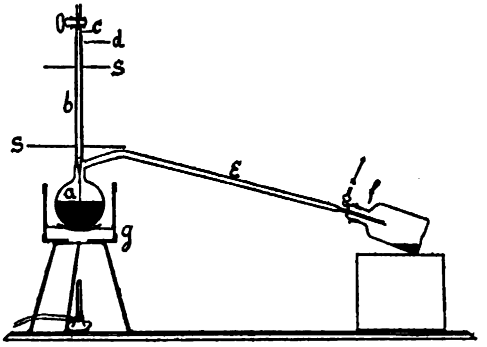


Fig. 1.

three hours. Steady gas and water pressures are desirable. It is best to avoid all organic matter, dust and fat. The ground joints may be readily made sufficiently tight by a little grinding with fine emery if they are not satisfactory to start with. The rubber joint at *d* never gives trouble if the tube fits well in the neck of the flask which is 20 or 30 cm. long.

In distilling large amounts of mercury we have found it necessary to use a larger still provided with an electric heater and arranged to permit of introducing mercury into the still during the distillation. The main features of the still we are using are represented by the sketch in Fig. 2. The flask *a* is about 15 cm. in diameter and into the bottom is sealed the glass tube *e* which connects with the reservoir *h*. The cock *g* is ordinarily open but is often found to be necessary. It was found that the air might be admitted from below through the side tube *s* instead of from above through the neck as in the proceeding still. *f* is a ground glass joint, the tube ends in a capillary which delivers the air well into the tube *e* where it bubbles up through the mercury and into the still. With this arrangement one can always observe the rate at which the air is passing into the mercury and control it with the cock *i*. Mercury is allowed to flow into the reservoir *h* at any desired rate and this controls the rate at which the mercury enters the flask *a*. The mercury vapor is condensed in the large "U" tube *c*, *c* which is made from 25 mm. thin-walled tubing and is 50 cm. long, thus giving a condensing tube one meter long. The tube *o* is joined to a Sprengle suction pump and manometer and a vacuum of 20 to 30 mm. maintained in the apparatus during distillation. The mercury condenses in the tube *c*, *c* and collects in the tube *d* and flows out at the bent up end. This tube *d* is about a meter long and 4 mm. in diameter.

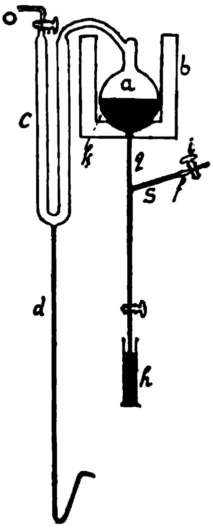


Fig. 2.

b, *b* is an electric heater made from asbestos, water glass and magnesium oxide cement. The heating coils are of "nichrome" ribbon and are located on the sides and bottom. The bottom part of the still is made from strips of asbestos 40 mm. wide and 1.5 mm. thick. The nichrome ribbon is placed along the edge of these strips and then they are rolled up together forming the ribbon into a spiral very close to one side of the " wheel " formed. The asbestos strips are well wetted with water and the waterglass-magnesium oxide mixture and after it is wound it may, while still wet, be dished to fit the form of the bottom of the flask. This gives a good support to the flask and the heating coil is right where it will be most effective. A short piece of brass tubing is attached to the end of the nichrome ribbon as a convenience in starting the roll. This brass tube serves as a hole for the tube *e* and also as one terminal for this heating coil. For 110-volt circuits this coil should have a resistance from 12 to 15 ohms.

A thin piece of asbestos is wound on a cylindrical form of the desired diameter. The asbestos "wheel" just made is forced into one end of the cylinder and on the outside is wound nichrome ribbon to form the heater for the sides, about 5 or 6 ohms are needed here. About the cylinder is wound a layer of asbestos wet with the cement and over all several layers of asbestos for insulation. The top of the heater is also covered with asbestos and glass wool. Some more resistance will be needed if all the heat from the 110-volt circuit is to be used in the heater. This is easily accomplished by making a spiral of nichrome wire and placing it in the lower inside corner of the heater *k*, *k*. The resistance of this coil may be adjusted so that no external resistance need be used and when working normally the rate of distillation should be such that the mercury vapor is condensing over nearly the whole length of the condenser. Our still takes 4.6 amperes at 110 volts and distills about two kilograms an hour. The electrical energy used is thus about half a kilowatt hour for two kilograms of mercury and at the high rate of 10 cents per kilowatt hour this would cost only 2½ cents a kilo for the electrical energy. If the heat needed to evaporate a kilo of mercury is 62,000 calories it would seem that only about one third of the heat generated by the current was used in volatilizing mercury. The still needs little attention when once in operation and will easily distill 20 kilos a day.

This apparatus is fastened to an upright support which is part of a large tray, a bracket holds the heater. After using the still the last of the mercury is run out and acids drawn up into the flask *a* and the condensing tube if necessary. One to one nitric acid is best for this purpose and is followed with distilled water. The still is easily cleaned and dried without dismantling. The glass cocks should be well ground so as to avoid the use of fat or organic matter, the cocks need not be perfectly tight. In constructing and assembling this apparatus a hand blowpipe was found to be indispensable.

Princeton, N. J.,
July, 1911.

THE EXCEPTION TO HOOKE'S LAW.

By Julian C. Smallwood.

THE phenomenon which it is the purpose of this article to describe was first observed by the writer during an investigation (still in progress) of the drum motion of a steam engine indicator. This motion is not exactly proportional to that of the steam engine cross-head because of the stretch of the cord transmitting it. The stretch, of course, depends upon the stress existing in the cord, and as the stress varies from point to point of the motion cycle, there are errors in the indications of the instrument. In the primary investigation, the problem was attacked by first obtaining autographic diagrams of the cord stress. The cord was then tested for the relation between stress and strain under static conditions. This test was made by *adding* dead weights and measuring corresponding elongations, but no measurements were made under decreasing loads. The result was a confirmation of Hooke's law. Other experiments, however, indicated that this law did not obtain. It occurred to the writer that perhaps a different law governed the relation between stress and strain when the stress was rapidly varied. So an experiment was devised by which an autographic stress-strain diagram could be secured under the condition of rapid motion.

The apparatus is shown by Fig. 1. It consists of a reciprocating cross-head, *C*, carrying a bell-crank lever, *L*, to the short arm of which is attached a spring by means of a spindle, *S*, the spring being mounted on the cross-head. The other arm carries a pencil point which traces the diagram upon a stationary slip of paper, *P*. In operation, a long cord, *K*, is attached to the spindle at one end, the other being tiedto a stationary point. As the cross-head reciprocates, the string is stretched in amounts nearly equal to the horizontal motion of the pencil. The stress in the cord is transmitted to the spring which elongates or contracts accordingly, such elongation or contraction giving a corresponding vertical motion to the pencil point. This motion is roughly proportional to the stress causing it. The cross-head being reciprocated, there results a stress-strain diagram under the

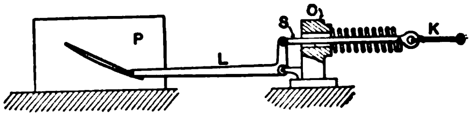


Fig. 1.

desired conditions, which may be corrected vertically for the kinematic error of the bell-crank and horizontally for the stretch of the spring.

Fig. 2 is such a diagram, corrected, and reveals an unexpected result. As the stress increases, the stretch varies directly with it, but, in decreasing, this relation no longer holds. The curve representing the decreasing values approximates to a circle. The cord does not return to lengths corresponding to the previous stresses except at the initial load. Upon being stressed again with first increasing and then decreasing force the identical variation is repeated.

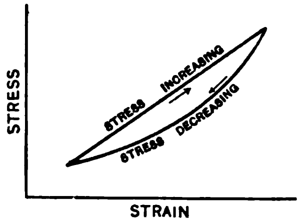


Fig. 2.

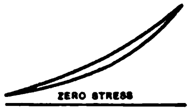


Fig. 3.

Fig. 3 is a copy of an actual record which was taken in order to determine if the relation between stress and strain was at all dependent upon the speed of application of the stress. The oscillation of the cross-head was first made very slowly (about 10 seconds in duration) and a diagram recorded. The speed was then increased to about 100 oscillations a minute and another diagram recorded on the same paper. This procedure was repeated, the speed being varied up and down for five minutes from very slow to 600 oscillations a minute, and occasional diagrams taken. No matter what the speed, the pencil traversed the same curve with remarkable precision, whatever blurring of the lines that occurred being due to the violent swaying of the cord at the high speeds. The curvature of the upper line of Fig. 3 is due to the kinematic error of the bell crank, previously mentioned. When this is allowed for, the ascending curve becomes straight.

The original record is a combined stress-strain diagram of the cord and spring. The stretch of the spring, however, was small compared with that of the cord, so its influence to alter the relation sought was probably slight. But, to be sure that the inertia or the friction of the link work of the recording mechanism did not cause a false record, a static test was made in this manner. Fifteen feet of previously stressed cord was hung and a scale poise tied to its lower end. One pound weights were placed successively upon this poise and the corresponding cord elongations measured, the time intervals between the additions of weight being constant, fifteen seconds. The weights were then removed in the same way and the elongations under decreasing loads recorded. When the results were plotted, the same character of curve appeared as in the motion tests, and showed practically the same relation quantitatively.

By another device, similar in principle to Fig. 1, were obtained superposed diagrams for various ranges of stress. Fig. 4 is such a one, corrected. Upon increasing the stress from zero to four and one half pounds, decreasing to three, and then increasing again to four and one half pounds, the curve traversed is *0abcda*. Similarly for the other ranges of stress. It is seen that the higher the stresses limiting a given range the less is the stretch produced in that range, that the ascending curves are all straight lines although of different slopes; and that the descending curves are arcs.

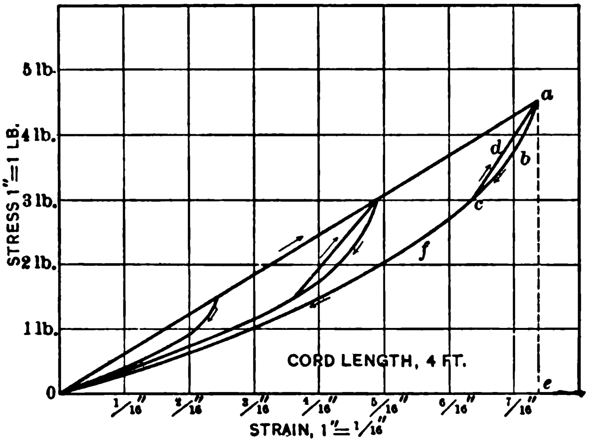


Fig. 4.

The following explanation of the departure from Hooke's law is so obvious that it seems remarkable it was not foreseen. In Fig. 4, the area *0ae* is a work diagram, being the product of force and distance. This area represents the work done on the cord. Now, when the force is decreasing, the cord shortens because of the tension of its fibers, and therefore performs work. This is represented by the area *0fae*. If the stress curve returned upon the same line as that upon which it advanced, the one area would equal the other; that is, the work delivered by the cord would be equal to that done upon it. This would be equivalent to the operation of a perfect machine, one having one hundred per cent. efficiency, which is impossible. The area *0af0* measures the lost work caused by the friction of the fibers of the material.

This physical property, it will be noted, resembles the magnetic one known as hysteresis. As the physical property is due to the reluctance of the fibers to return to their original shape, the term "lag" is perhaps an appropriate name for it.

There is nothing to indicate that the reasoning just given applies only to a woven fabric like indicator cord. Although the phenomenon of lag has a decided bearing upon the records of a steam engine indicator, its chief importance may lie in its occurrence in other materials. In view of the fact of molecular friction which is exerted when any material changes shape, this property *must* be a characteristic of *all* materials· If Hooke's law obtains with increasing stress, it cannot do so when the stress decreases. Following this conclusion, many interesting conjectures may be made regarding the result of lag upon the records of instruments of precision, especially those dependent upon springs. Theoretically. such instruments, if indicating correctly upon an increasing scale, cannot do so when the measured quantity decreases. The question at once suggests itself, is the departure of the two scales sufficiently marked to receive serious attention?

The writer has made some experiments upon springs with the purpose of answering this question. The results, however, were not sufficiently reliable to quote, the apparatus being crude, but it may be said that the up and down curves did not appear to vary materially.

On the other hand, the writer has tested a transmission power dynamometer (depending upon the twist of a spring for its indications) and discovered a difference of about two per cent. at the maximum between the up and down scales. It should be noted however, that this difference must have been due not only to the internal friction of the spring but, in part, to that of a roller bearing which supported the shaft delivering the power.

It is recognized that, in the calibration of an indicator spring, it is necessary to obtain two scales, one for ascending, the other for descending pressures. The differences between these scales have generally been attributed to the friction of the indicator piston in its cylinder and of the joints of the pencil motion. It is possible that they are also due to the molecular friction of the spring.

An occurrence was related to me by an eminent engineer which illustrates in an interesting way the effect of lag upon an instrument of precision. This gentleman had several very sensitive aneroid barometers which he wished to test. Having occasion to take a railroad journey which necessitated crossing a mountain, he took along his barometers, and, as the ascent, was made, compared their indications. These coincided very closely. But, upon descending, he found them very much at variance. The barometers were quite differently constructed, especially as to moving parts, so he concluded that it was the internal friction, being different in amount in the different instruments, which caused their lack of harmony. In his own words, "Those that had the greatest friction needed more *time* to come back." But, as the writer has pointed out, the phenomenon of lag, at least as manifested by cord, is independent of the element of time.

Another interesting result of lag is the consequent variation in the coefficient of elasticity. Instead of being a constant, this quantity depends upon the range of stress as shown by Fig. 4. Whether or not its variation is material, in the case of metals, is open to investigation.

Further, the question of the *efficiency* of materials may be worthy of investigation. It appears that the true measure of the resilience of a material is the product of the work done upon it and its efficiency, this product being equal to the work returned by the material as its fibers resume their original shape. Is this efficiency constant or does it vary with the range of stress?

It may be that the phenomenon of lag has more claim upon academic than practical interest, and that its effect upon precision measurements, as far as molecular friction is concerned, is trifling. At all events, it seems worth while to investigate further whether or not this is the case.

A SIMPLE PROOF OF POYNTING'S THEOREM.

By J. F. H. Douglas.

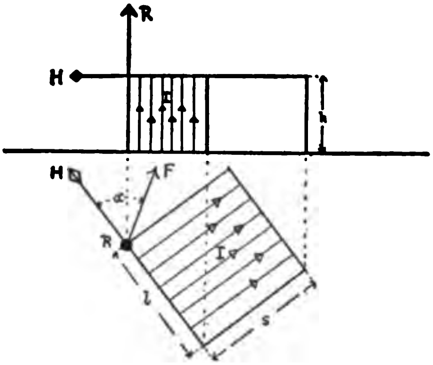
POYNTING'S theorem, which states the law which electrical energy observes in its flow through space, offers some difficulties to a beginner. In the case of a direct-current circuit everything in space outside of the wire seems to be static, and power without motion is hard to conceive. Moreover, the mathematical proof usually given is not simple enough to suggest any mechanism by which the power flow can take place. The result also is uncertain by a function which would integrate to zero over the boundary of the region considered.

If power is actually flowing through space, so that it enters some sides of a box cut out of space and leaves others, the fact is obscured by the apparent absence of any action of the particles inside the box upon the particles outside the same. If, however, we could isolate an element by any means from its neighbors, the power flow should be apparent at the boundaries. Thus where power was entering the element there should be a source of energy, and where the power was leaving the element there should be a consumption of energy.

The magnetic field within any tube of magnetic force may be considered as due to a current circulating around it. This current will have the same number of ampere-turns as the current in the conductor which produces the field. Such a combination is equivalent to the original one; for, if combined, the currents would all cancel each other outside the conductors. Moreover, if the currents are distributed in proportion to the intensity of the field, each current would produce no action outside the tube it surrounds. Thus the current wrapping for a given element would be adequate to produce the magnetic field within it. The element being shielded from magnetic forces, the only work done at the boundaries must be electrical work. Therefore, this must be done by virtue of the electric field. The current, which we suppose to circulate around each tube of force, in some places flows against and in some places with the electric field. Hence, in some places energy is leaving the electric circuit for the interior of the element; and on the opposite side, while flowing in the same direction, leaves the element for the electric circuit. Thus, the desired isolation is secured, and the action at the same time is seen to be a dynamic and not a static one.

Poynting's theorem states that energy flows in a direction perpendicular to both the electric and the magnetic fields. It is natural, therefore, to take as our element a portion of a tube of magnetic force bounded by surfaces in the plane of the magnetic and electric fields, and by surfaces perpendicular to this. Referring to the sketch we shall see, that in order to produce an internal magnetic field of H ampere-turns per centimeter, we need a current around the box of

$$I = H \times l \text{ amperes.} \qquad (1)$$



An Element of the Electromagnetic Field Showing the Flow of Power.

This current flows at right angles to the electric field on the two sides of the box and hence does no work there. It flows with the electric field on the top of the box and against it on the bottom of the box. Electrical energy is being consumed on the lower or "motor" side to supply the energy which flows upward. This energy reappears as electrical energy on the top or "generator" side. The work done on either face is EI watts where E is the voltage drop across the face of the element. But

$$E = F \times s \times \text{Sin } \alpha \text{ volts,} \qquad (2)$$

where F is the number of volts per centimeter. Hence the power

$$W = E \times I = F \times H \times (\text{Sin } \alpha) \times s \times l \text{ watts,} \qquad (3)$$

and the power flow per square centimeter is

$$R = W/(s \times l) = F \times H \times \text{Sin } \alpha \text{ Watts per sq. cm.} \qquad (4)$$

This is Poynting's theorem. Although the proof is given in the practical units, it would have been just as easy to use the C.G.S. units instead.

The similarity of magnetic circuit relations to those of the electric circuit permit us to speak of magnetic "current" and magnetic power.[1] We could, therefore, have isolated our elements by wrapping the tubes of electric force with magnetic currents. The proof in this case would have been just as direct. However the assumption of electric currents was chosen as the more natural.

It could be proved, along lines similar to those above, that the energy flow given by equation (4) will account exactly for the increase or decrease in the energy within any volume. There would be no point in doing so for two reasons. First, although perhaps somewhat shorter than most proofs, it would really be the same as that usually given as a proof of Poynting's theorem.[1] Second, such a proof would seem unnecessary when once we concede that the energy does flow according to the above law (Eq. 4).

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[1] See Oliver Heaviside, *Electromagnetic Theory* (1893), Vol. I, p. 25.

The generality of the proof given here deserves some further consideration. Since the method used does not depend upon a surface integration, there is not that uncertainty in the proof, which always goes with the attempt to find the integrand which gives a certain integral. Moreover, the mathematics are so simple, that chance for ambiguity in other directions is hard to see. Thus any limitations as to the definiteness of the result should lie in the physical conceptions here presented and not in the mathematics. The writer believes that the assumptions are at least natural, and that the proof helps to make the rationale of the process of energy flow plain.

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[1] For example see that in Dr. J. G. Coffin's *Vector Analysis*, pp. 164–165.

Volume XXXIII. *November, 1911.* *Number 5*

THE

PHYSICAL REVIEW.

AN ABSOLUTE DETERMINATION OF THE MINIMUM IONIZING ENERGY OF AN ELECTRON, AND THE APPLICATION OF THE THEORY OF IONIZATION BY COLLISION TO MIXTURES OF GASES.

BY EDWIN S. BISHOP.

THE theory of "ionization by collision" has been very beautifully worked out by J. S. Townsend and verified by him and others[1] for various gases at low pressures. The orignial purpose of these experiments was to submit the theory to a more rigid test by extending the observations to wide ranges of pressure, and by predicting, if possible, the electrical properties of a mixture of gases, the properties of the constituent pure gases being known.

Professor Townsend has shown that an ion in a sufficiently strong electric field will acquire sufficient kinetic energy between some of the collisions with the molecules to produce new ions from the neutral molecules. He has further shown that if the field strength is not too high, it is only the negative ion which is effective in producing new ones. Under these conditions, if we have n_0 ions set free by the action of the ultra-violet light at the negative plate of the two parallel plates between which the electric field is established, then the number of ions n reaching the positive plate is given by the formula

$$n = n_0 e^{\alpha d} \tag{1}$$

where e is Napier's base, α is the number of ions (either positive or negative) produced by the collisions of a negative ion in passing through one centimeter of the gas, and d is the distance between the plates in centimeters. Townsend[1] has also shown that for large values of X/p (field strength in volts per cm. ÷ pressure), the positive ions also produce new ones by collision, so that if β is the number of ions (either positive or negative) produced by a positive ion in passing through one centimeter of the gas, then the number of ions n which reach the positive plate is given by the equation

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[1] Townsend, Nature, Vol. LXII., Aug. 9, 1900; Phil. Mag., Feb., 1901, June, 1902, Nov., 1903, March, 1905; Townsend and Kirkby, Phil. Mag., June, 1901; Townsend and Hurst, Phil. Mag., Dec., 1904; Hurst, Phil. Mag., April, 1906; Gill and Pidduck, Phil. Mag., Aug., 1908.

$$n = \frac{n_0(\alpha - \beta)e^{(\alpha-\beta)d}}{\alpha - \beta e^{(\alpha-\beta)d}}.$$

Inasmuch as all the experiments herein described were carried out at pressures much higher than those used by Townsend, the values of X/p are comparatively small, and consequently the first formula $n = n_0e^{\alpha d}$ was found to satisfy all of the experimental data.

Description of Apparatus.

The apparatus which was used for finding the conductivity between two parallel plates is shown in Fig. 1. The conductivity was started by means of ultra-violet light falling upon the aluminum plate B, from the spark S, which consisted of two zinc electrodes. The spark was maintained by the discharge of four Leyden jars across the secondary of a Scheidel induction coil. The Scheidel coil was run on an alternating current from a rotary generator, the current which supplied the coil being

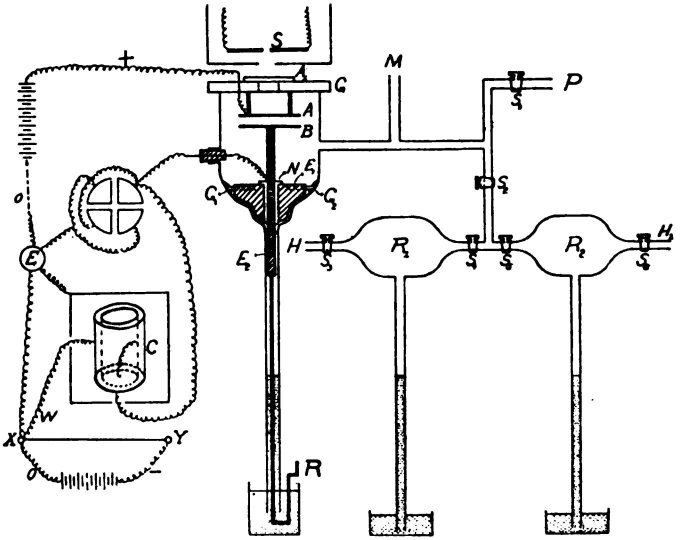

Fig. 1.

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[1] Townsend, Phil. Mag., Nov., 1903.

kept constant throughout a set of readings as well as the speed of the rotary generator. In this way the intensity of the light from the spark could be kept at any desired value, and a set of readings could be reproduced at any time with an error of less than three per cent. The ionization of the gas took place between the plates A and B, which were five centimeters in diameter. Plate G was a piece of heavy plate glass with a circular aperture one centimeter in diameter, over which was cemented the quartz plate A_1. Plate A was a silvered quartz plate with lines ruled every four tenths of a millimeter over an aperture one centimeter in diameter, to allow the passage of the light. Plate B was made of aluminum, mounted on a metallic screw which turned in the metal nut N, by means of the rod R. E_2 was a piece of ebonite about three centimeters long inserted between the screw and the rod to secure insulation. E_1 was an ebonite base which was held firmly in place by inserting into it glass rods, G_1, G_2 (G_3 not shown in diagram), which were fastened to the sides of the glass ionizing chamber with cæmentium. Plate B was made as accurately parallel with plate A as was possible before fastening plate G, which carried plate A by means of pillars, to the ionizing chamber. Plate G was sealed to the apparatus with De Khotinski cement. Connection was made between the plate B and the electrometer by a wire passing from the nut N through an amber plug in the side of the ionizing chamber. C was a cylindrical condenser the inside of which was connected to the plate B and the electrometer, and the outside of which was connected by the slide wire W to a high resistance bridge XY to which was applied about six volts for the measurement of the smaller currents. The positive potentials applied to the plate A were obtained from storage batteries, and varied from fifty to thirty-four hundred volts, depending on the pressure of the gas. These voltages were read on one of four Kelvin and White static voltmeters which ranged from 0 to 90 volts, 0 to 360 volts, 0 to 900 volts, 0 to 1,600 volts respectively. The voltmeters were first accurately calibrated by Mr. Kadesch and myself with a standard voltmeter, and were accurate to within one half per cent. A Gaede pump attached at P served to evacuate the whole system. A MacLeod gauge attached at M was used to measure pressures up to four centimeters. The higher pressures were read directly from a mirror scale placed back of the tube M. R_1 and R_2 were glass reservoirs of about 500 c.c. capacity which contained the gases to be studied. R_1 was kept nearly filled with hydrogen throughout the course of the experiments. The hydrogen used was produced by the electrolysis of phosphoric acid in distilled water. It was then bubbled through an alkaline solution of pyrogallic acid to remove the oxygen and passed into three drying tubes which contained caustic potash, calcium chloride, and phosphorous pentoxide respectively. All connections for this system were glass-sealed joints. After staying in the drying tubes for at least eight hours, the hydrogen was admitted to the reservoir R_1. The reservoir R_2 contained either air or else carbon dioxide, depending on the gas or mixture being studied. The carbon dioxide was carefully prepared and dried, as was also the air. The volumes of R_1 and R_2 were accurately determined before setting up the apparatus by weighing each empty and then filled with water at a known temperature. The barometer tubes leading down from R_1 and R_2 were each provided with a scale so that by knowing the change in pressure and volume of each reservoir, the quantity of each gas which was admitted to the ionizing chamber was known with an accuracy of one tenth per cent. The ionizing chamber for each set of observations was first exhausted to a pressure of one thousandth of a millimeter or less, with the Gaede pump, and then filled with a fresh supply of gas to a pressure which was always about ten centimeters greater than that for which the observations were to be taken. The ionizing chamber was then exhausted to the desired pressure. By this means, the traces of any gas left could never have been more than one hundred-thousandth part of the whole, and would therefore produce an entirely negligible effect. The apparatus was tested several times during the course of the experiments and when exhausted to one thousandth of a millimeter or less, the increase of pressure during three hours, the time required to make a set of observations, was never found to be more than two thousandth of a millimeter, so that any impurities in the gas arising from leakage or occluded gases in the apparatus must have produced an entirely negligible effect.

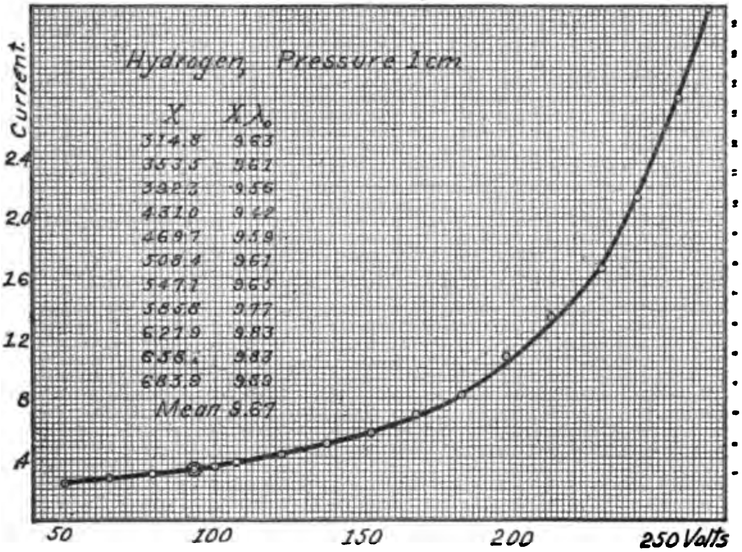
METHOD OF OBSERVING.

To make an observation the desired positive potential was applied to plate A; plate B, the pair of quadrants to which B was connected, and the inside cylinder of the capacity were earthed, and the slide wire W was at X (always zero potential). The spark was then started, plate B and its connecting system unearthed, and the time noted with a stop watch which was required for B to acquire a positive charge which could be just balanced by sliding the wire W of the inductive balance from X to Y. By this means the deflection of the electrometer could be kept within a fraction of a millimeter of its zero point, at a distance of 150 cm., during an observation. Three trials were usually made for an observation, the individual trials seldom varying by more than two per cent. from the mean.

To obtain a set of data the above process was repeated for several positive potentials applied to plate *A*, starting with potentials considerably less than was required to produce ionization by collision and continuing up to voltages which produced ionization currents that could just be balanced on the bridge.

If we let *V* represent the P.D. across the inductive balance, *c* the capacity of the condenser, electrometer, and plate *B*, and *t* the time in seconds required for plate *B* to acquire the potential *V*, then the currents through the gas will be proportional to cV/t. Since the capacity is constant the currents will be proportional to V/t, and these are the values for the current which are given in Figs. 2 to 10 inclusive.

It will be noted from the figures that the so-called saturation current slowly increases with the potential applied to plate *A* until the field strength (potential ÷ distance between plates) is sufficient to produce new ions by collision, at which point the increase in current becomes much greater. Before that field strength is reached, equal small increments in current are produced by equal large increments in the potentials applied to plate *A*, giving a straight line when plotted up to the point where ionization by collision begins. This gradual increase in the so-called saturation current is probably due to two causes. First, as the field strength is increased, fewer of the electrons released by the action of the light are discharged back to the plate, and second, the energy of emission of the electron from the plate added to the energy it received



X	Xλ₀
314.8	9.63
353.5	9.61
392.3	9.56
431.0	9.42
469.7	9.59
508.4	9.61
547.1	9.65
585.8	9.77
621.9	9.83
656.4	9.83
683.9	9.80

Mean 9.67

Fig. 2.

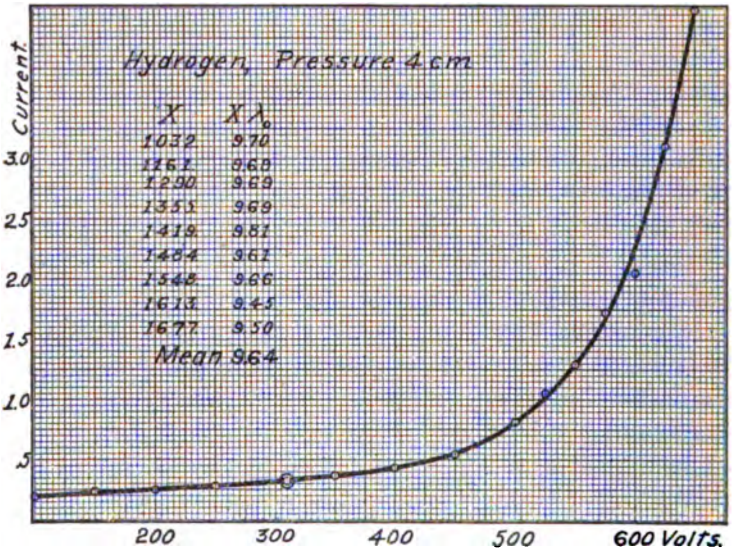

Hydrogen, Pressure 4 cm
X Xλ₀
1032 9.70
1161 9.68
1290 9.69
1355 9.69
1419 9.81
1484 9.61
1548 9.66
1613 9.45
1677 9.50
Mean 9.64
Current.
3.0
2.5
2.0
1.5
1.0
.5
200
300
400
500
600 Volts.

Fig. 3.

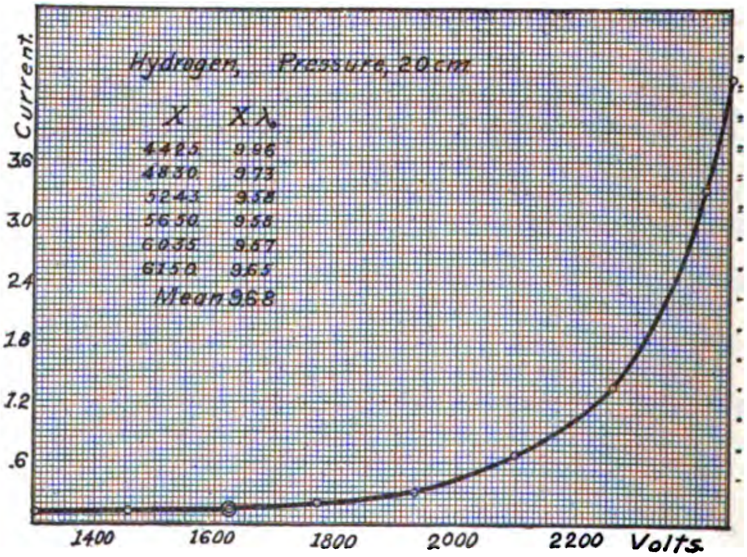

Hydrogen, Pressure, 20 cm
X Xλ₀
4425 9.96
4830 9.73
5243 9.58
5650 9.58
6035 9.67
6150 9.65
Mean 9.68
Current.
3.6
3.0
2.4
1.8
1.2
.6
1400
1600
1800
2000
2200 Volts.

Fig. 4.

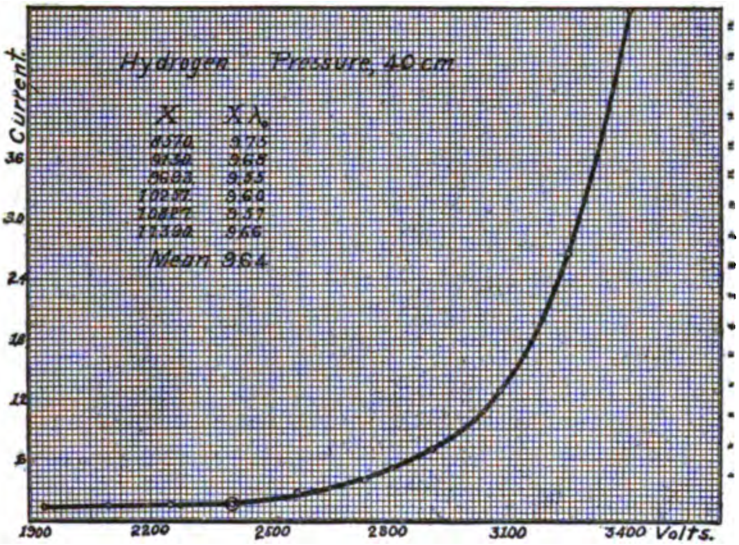

Hydrogen Pressure, 40 cm
X Xλ_0
8570 9.75
9130 9.68
9693 9.55
10237 9.60
10827 9.57
11398 9.66
Mean 9.64
Current
36
3.0
2.4
18
12
6
1900
2200
2500
2800
3100
3400 Volts.

Fig. 5.

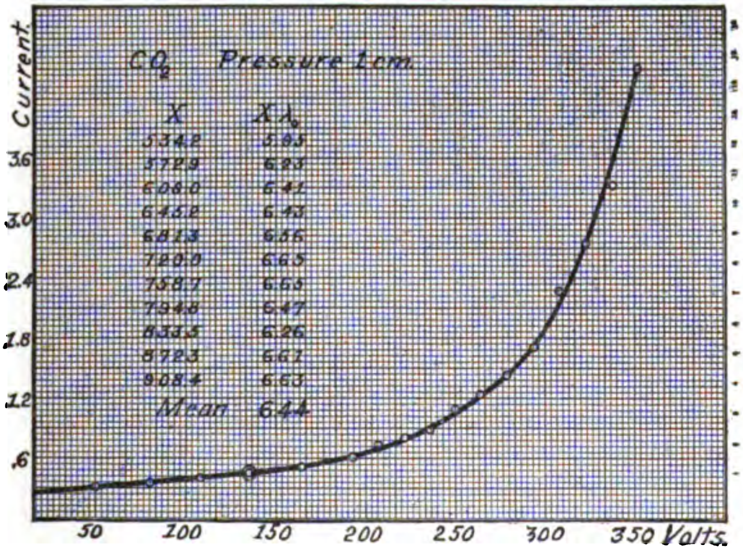
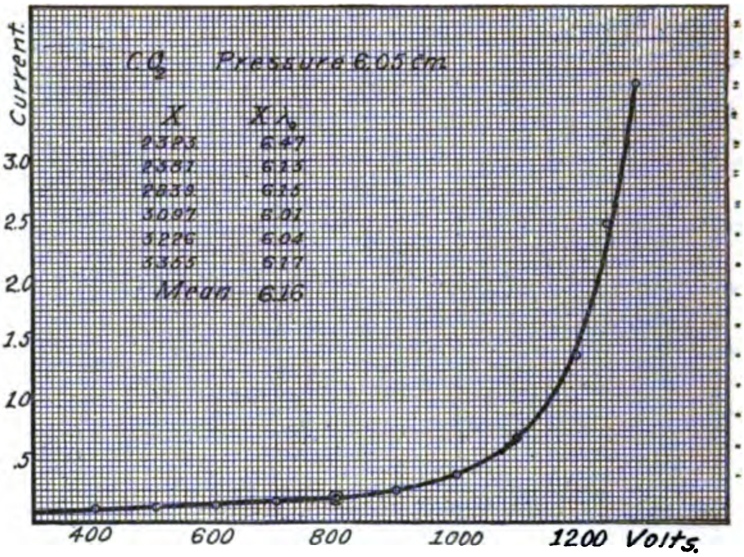
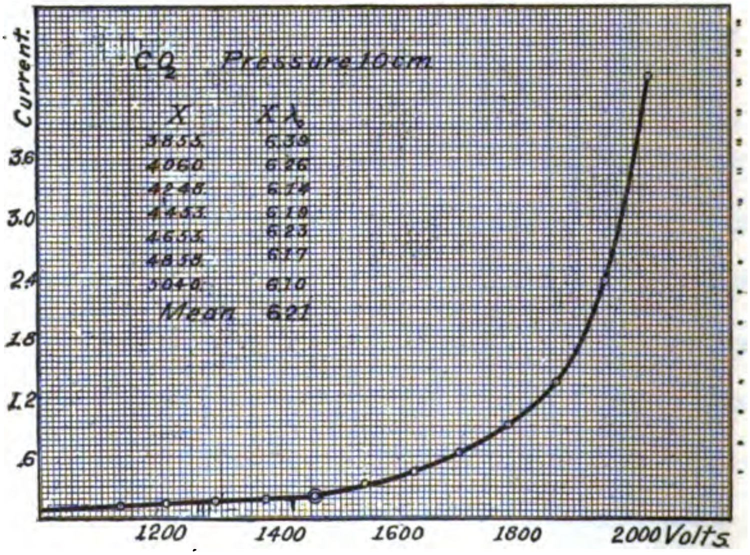

CO_2 Pressure 1 cm.
X Xλ_0
534.2 5.85
572.9 6.23
608.0 6.41
646.2 6.43
681.3 6.56
720.0 6.65
758.7 6.65
794.8 6.47
833.5 6.26
872.3 6.61
908.4 6.63
Mean 6.44
Current
3.6
3.0
2.4
1.8
1.2
.6
50
200
150
200
250
300
350 Volts.

Fig. 6.



X	$X\lambda_0$
2323	6.47
2387	6.25
2839	6.15
3097	6.01
3226	6.04
3365	6.17
Mean	6.16

Fig. 7.



X	$X\lambda_0$
3855	6.39
4060	6.26
4248	6.14
4453	6.19
4653	6.23
4858	6.17
5040	6.10
Mean	6.21

Fig. 8.

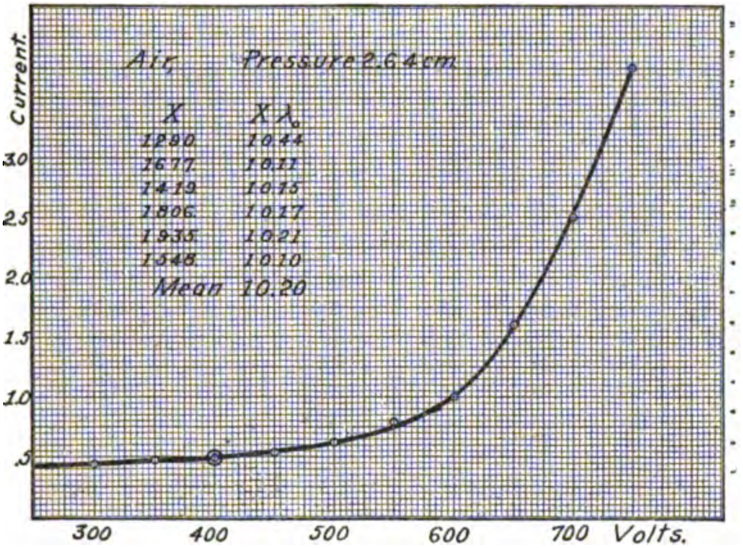

Current.
Air, Pressure 2.64 cm
X Xλ₀
1290 10.44
1677 10.11
1419 10.15
1806 10.17
1935 10.21
1548 10.10
Mean 10.20
3.0
2.5
2.0
1.5
1.0
.5
300
400
500
600
700
Volts.

Fig. 9.

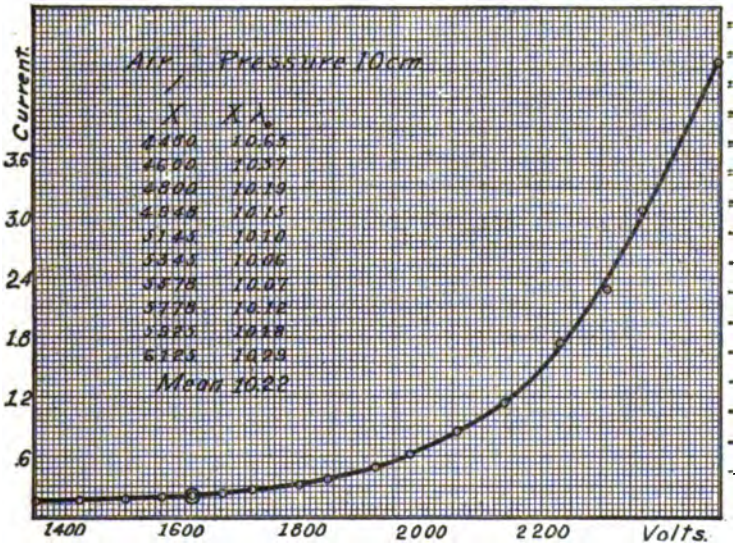

Current.
Air, Pressure 10 cm
X Xλ₀
4450 10.65
4600 10.37
4800 10.19
4848 10.15
5145 10.10
5345 10.06
5576 10.07
5776 10.12
5825 10.18
6125 10.29
Mean 10.22
3.6
3.0
2.4
1.8
1.2
.6
1400
1600
1800
2000
2200
Volts.

Fig. 10.

Table I.

Hydrogen.

Pressure 1 cm.
$n_0 = .345$, $d = .3875$ cm.

X	n/n_0	a	X'
314.8	1.245	.544	312.0
353.5	1.435	.932	356.3
392.3	1.640	1.277	390.1
431.0	2.010	1.802	435.3
469.7	2.390	2.249	469.8
508.4	3.130	2.945	518.4
547.1	3.880	3.499	554.9
585.8	4.840	4.070	590.0
621.9	6.200	4.710	626.6
658.1	8.120	5.404	664.5
683.9	9.920	5.923	691.0

Pressure 4 cm.
$n_0 = .323$, $d = .3875$ cm.

X	n/n_0	a	X'
1,032	1.32	.716	1,025
1,161	1.69	1.360	1,157
1,290	2.51	2.375	1,273
1,355	3.26	3.050	1,352
1,419	3.92	3.525	1,404
1,484	5.32	4.314	1,485
1,548	6.34	4.766	1,528
1,613	9.60	5.837	1,625
1,677	13.10	6.632	1,694

Pressure 20 cm.
$n_0 = .123$, $d = .4$ cm.

X	n/n_0	a	X'
4,425	1.56	1.112	4,546
4,830	2.43	2.220	4,838
5,243	5.32	4.179	5,239
5,650	10.97	5.981	5,548
6,035	26.90	8.220	5,884
6,150	35.90	8.942	5,982

Pressure 30 cm.
$n_0 = .130$, $d = .3$ cm.

X	n/n_0	a	X'
6,543	1.67	1.709	6,696
6,997	2.43	2.960	6,977
7,503	3.84	4.485	7,264
8,020	6.96	6,467	7,586
8,580	13.65	8.702	7,906
9,100	33.98	11.740	8,293

Pressure 1.9 cm.
$n_0 = .318$, $d = .3875$ cm.

X	n/n_0	a	X'
451.6	1.11	.269	472.6
516.1	1.23	.534	521.5
580.6	1.45	.959	583.1
645.2	1.74	1.430	639.9
709.7	2.29	2.138	714.0
774.2	2.97	2.810	775.2
838.7	4.03	3.597	840.9
903.2	5.66	4.472	906.9
967.7	8.01	5.370	971.3
1,032.2	11.48	6.292	1,031.3
1,058.0	13.43	6.697	1,057.4

Pressure 5 cm.
$n_0 = .481$, $d = .3875$ cm.

X	n/n_0	a	X'
1,161	1.16	.383	1,166
1,290	1.45	.962	1,294
1,419	1.83	1.564	1,398
1,548	2.61	2.476	1,529
1,677	4.17	3.685	1,676
1,806	6.65	4.889	1,805
1,871	9.16	5.716	1,887

Pressure 10 cm.
$n_0 = .176$, $d = .3875$ cm.

X	n/n_0	a	X'
2,323	1.38	.831	2,350
2,581	1.94	1.710	2,547
2,839	3.31	3.089	2,789
3,097	6.40	4.790	3,035
3,226	9.37	5.773	3,161
3,355	14.27	6.852	3,293
3,484	23.50	8.13	3,436

Pressur o cm.
$n_0 = .141$. $d = .3$ cm.

X	n/n_0	a	X'
8,570	1.87	2.086	8,877
9,130	2.68	3.286	9,164
9,693	4.93	5.318	9,568
10,257	9.15	7.379	9,919
10,827	18.78	9.765	10,284
11,390	36.09	11.940	10,586

from the field would be sufficient to ionize at the first impact, although the field strength were below the minimum ionizing field strength. When, however, the field strength attains such a value that the electron acquires sufficient energy between some of the impacts to ionize, then the current will increase rapidly for small increases in field strength. Thus the potential (or field strength) at which ionization by collision begins is obtainable either from the data or the curves and these points are indicated on the curves by two concentric circles. All the data for these experiments is obtainable from the curves, the abscissæ representing the number of volts applied to plate *A* and the ordinates representing the corresponding values of V/t (volts applied to inductive balance XY $\div$ time for plate *B* to acquire the potential V). The tables accompanying the curves show the values obtained for the ionizing energy for corresponding values of the field strength. The value of n_0 in all cases was taken as the value of the current at these doubly circled points, and n was the value of the current for any higher potential. The method of determining the minimum ionizing energy $X\lambda_0$ (free fall of the electron in volts) is given in the next general heading of this paper.

The values of α for various field strengths X were then calculated

Table II.

Carbon Dioxide.

Pressure 1 cm.
$n_0 = .453$, $d = .3875$ cm.

X	n/n_0	α	X'
534.2	1.60	1.213	553.7
572.9	1.79	1.503	583.8
609.0	1.95	1.733	605.4
645.2	2.43	2.291	656.9
681.3	2.73	2.591	682.4
720.0	3.16	2.970	713.2
758.7	3.75	3.412	747.4
794.8	5.01	4.158	801.9
833.5	6.07	4.653	836.3
872.3	7.33	5.141	861.3
908.4	9.93	5.925	898.0

Pressure 10 cm.
$n_0 = .204$, $d = .4$ cm.

X	n/n_0	α	X'
3,855	1.60	1.175	3,983
4,060	2.16	1.975	4,146
4,248	3.19	2.900	4,329
4,453	4.51	3.766	4,474
4,653	6.62	4.725	4,621
4,858	11.60	6.120	4,819
5,040	21.66	7.680	5,023

Pressure 3.53 cm.
$n_0 = .197$, $d = .3875$ cm.

X	n/n_0	α	X'
1,548	1.59	1.197	1,558
1,806	3.22	3.017	1,810
1,935	5.00	4.152	2,009
2,064	7.97	5.357	2,066
2,194	12.48	6.508	2,177
2,258	18.73	7.554	2,272

Pressure 5 cm.
$n_0 = .240$, $d = .3875$ cm.

X	n/n_0	α	X'
2,052	1.60	1.213	2,122
2,263	2.53	2.395	2,316
2,472	4.17	3.683	2,491
2,681	7.04	5.038	2,655
2,888	14.80	6.947	2,862
2,942	18.75	7.556	2,923

Pressure 6.05 cm.
$n_0 = .189$, $d = .3875$ cm.

X	n/n_0	α	X'
2,323	1.31	.697	2,407
2,581	2.04	1.840	2,634
2,839	3.64	3.334	2,865
3,097	7.25	5.112	3,096
3,226	13.07	6.624	3,272
3,355	19.21	7.618	3,380

from the formula $n = n_0e^{\alpha d}$, and are given in Tables I., II., and III. The computed values of the field strengths X' required to produce the same current, *i. e.*, the same value of n/n_0 are given in the last columns of the same tables. The method of obtaining these will be described in a later section.

Table III.

Air.

Pressure 2.64 cm. $n_0 = .498$, $d = .3875$ cm.			
X	n/n_0	α	X'
1,290	1.25	.576	1,287
1,419	1.59	1.197	1,419
1,548	2.00	1.789	1,522
1,677	3.21	3.009	1,699
1,806	5.02	4.163	1,843
1,935	7.53	5.210	1,959
Pressure 4.92 cm. $n_0 = .155$, $d = .3875$ cm.			
2,323	1.43	.914	2,358
2,581	2.14	1.963	2,594
2,839	3.53	3.254	2,824
3,097	6.64	4.885	3,068
3,226	10.13	5.969	3,214
3,354	16.25	7.187	3,365
3,419	21.60	7.920	3,452

Pressure 10 cm. $n_0 = .197$, $d = .4$ cm.			
X	n/n_0	α	X'
4,480	1.56	1.112	4,576
4,600	1.86	1.551	4,709
4,800	2.46	2.250	4,892
4,948	3.13	2.852	5,033
5,145	4.28	3.635	5,200
5,345	5.78	4.386	5,348
5,578	8.83	5.445	5,542
5,778	11.57	6.114	5,656
5,925	15.58	6.857	5,778
6,125	23.20	7.851	5,933
Pressure 5.27 cm. $n_0 = .205$, $d = .3875$ cm.			
2,323	1.20	.471	2,365
2,581	1.68	1.332	2,613
2,839	2.48	2.344	2,825
3,097	4.02	3.592	3,042
3,355	7.90	5.334	3,301
3,484	15.90	7.130	3,535

Determination of the Minimum Ionizing Energy.

Mr. Bergen Davis[1] has deduced a theory for the minimum kinetic energy which a negative ion must have in order to ionize a molecule by impact. He has shown that if α is the number of ionizing impacts which a negative ion makes in passing through one centimeter of a gas, l is the mean free path of the ion, and λ_0 is the minimum path which results in ionization, then the number of ionizing impacts is given by the following equation:

$$\alpha = \frac{1}{l}e^{-\frac{\lambda_0}{l}}\left[1 + \frac{\lambda_0}{l}e^{\frac{\lambda_0}{l}}Ei\left(-\frac{\lambda_0}{l}\right)\right],$$

which may be written

$$\alpha l = e^{-\frac{\lambda_0}{l}} + \frac{\lambda_0}{l}Ei\left(-\frac{\lambda_0}{l}\right). \qquad (2)$$

---

[1] Bergen Davis, Physical Review, Jan., 1907.

The values of the ponential integral $Ei(-\lambda_0/l)$ were obtained by him from tables by Dr. W. Laska (Sammlung von Formeln). The values of αl and the corresponding values of λ_0/l as computed by Davis are given in Table IV.

TABLE IV.

λ_0/l	αl	λ_0/l	αl	λ_0/l	αl
.04	.8536	.4	.3893	4	.0032
.06	.804	.6	.2762	5	.00099
.1	.7247	.8	.2008	6	.00032
.14	.656	1.	.1485	7	.000142
.2	.574	1.5	.0731	8	.000034
.25	.518	2.	.0375	9	.0000114
.3	.496	3.	.0106	10	.00000387

These values were plotted on three large curves about thirty centimeters each way, using the values of λ_0/l for the abscissæ and the corresponding values of αl for the ordinates. By referring to these curves the value of λ_0/l corresponding to any experimental value of αl could be interpolated within a fraction of one per cent.

The values of the mean free paths of hydrogen, carbon dioxide, and air at 76 cm. pressure and 23° C. in all these experiments were taken to be .0000185, .00000654, and .00000983 cm. respectively. At other pressures the mean free paths were taken inversely proportional to the pressure. In all cases the mean free path of the negative ion (electron) was taken to be 5.65 times the mean free path of the gas molecule at that pressure. If the electron is negligible in size, then its mean free path would be four times that of the gas under the same velocity conditions. Since, however, the electron when in fields sufficiently strong to cause it to ionize, moves with a velocity of order higher than that of the molecules,[1] its mean free path should be $\sqrt{2}$ times as great on that account.[2] Thus the mean free path of the electron in a gas should be $4\sqrt{2}$ times the mean free path of the molecule of the gas.[1]

Using this value of l and the experimentally determined values of α (see Tables I., II., III.), the values of λ_0/l corresponding to the values of αl for the various field strengths were found from the curves previously described. The minimum ionizing energy expressed in the number of volts through which the electron must freely fall would then be

$$\text{Energy (Volts)} = \frac{Xl\lambda_0}{l} = X\lambda_0.$$

---

[1] From $e/m = 5.6 \times 10^{17}$ E.S.U. and equating $\frac{1}{2}mv^2$ to $Xe\lambda_0$, the minimum ionizing velocities of the electron in hydrogen, carbon dioxide, and air are 10^3, 4.3×10^3, and 4×10^3 times as great as the velocities of agitation of the molecules of these gases respectively.

[2] J. C. Maxwell, Phil. Mag., Ser. 4, Vol. 19, p. 29, 1860.

The data for the different gases is shown by the curves of Figs. 2 to 10 inclusive, and the results for $X\lambda_0$ corresponding to different values of X are shown in the tables accompanying those figures. A summary of all the values of $X\lambda_0$ for the different gases and pressures is given in Table V.

TABLE V.

Hydrogen.		Carbon Dioxide.		Air.	
Pressure in cm.	$X\lambda_0$	Pressure in cm.	$X\lambda_0$	Pressure in cm.	$X\lambda_0$
1	9.67	1	6.44	2.64	10.20
1.9	9.59	3.53	6.28	4.92	10.22
4	9.64	5	6.17	5.27	10.18
5	9.68	6.05	6.16	10	10.22
10	9.72	10	6.21		
20	9.68				
30	9.67				
40	9.64				

In finding the final mean of $X\lambda_0$ (Table VI.) for the different gases the above values of $X\lambda_0$ were given weights proportional to the pressures, since the accuracy of several observations increases with the pressure. The value of the minimum ionizing energy expressed in ergs would be

$$\text{Energy (Ergs)} = \frac{X\lambda_0}{300}\cdot e,$$

where e is the value of the elementary charge on the electron. The value of e used here was 4.89×10^{-10}, which was the value recently determined by Professor R. A. Millikan[1] by experiments on oil drops and which has been verified by E. Regener.[2]

TABLE VI.

Gas.	$X\lambda_0$ (Volts).	$Xe\lambda_0$ (Ergs).
Hydrogen	9.66	1.58×10^{-11}
Carbon dioxide	6.21	1.01×10^{-11}
Air[3]	10.21	1.67×10^{-11}

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[1] R. A. Millikan, Science, Vol. XXXII., Sept. 30, 1910, and PHYSICAL REVIEW, April, 1911.

[2] E. Regener, Physikalische Zeitschrift, Feb. 15, 1911.

[3] The mean free paths used in determining the above values were taken from Meyer's Kinetic Theory. The mean free path of air at 23° C., computed from the most probable value of the coefficient of viscosity as given by R. A. Millikan in the PHYSICAL REVIEW, April, 1911, p. 386, is 5 per cent. less. This value of the mean free path of air gives a value for the ionizing energy which is 4 per cent. less than the above, or 9.8 volts. It will be noticed that O. V. Baeyer's value of 10 volts, which is the most direct determination which has been made, lies between these two values. This would indicate that Jean's correction for the persistence of velocities is not here needed.

Lenard,[1] by a very direct method obtained 11 volts for the ionizing energy of air, and O. v. Baeyer[2] by a similar direct method obtained 10 volts. For a review of other work on this subject the reader is referred to an article by Dr. Kleeman, published in the Proceedings of the Royal Society, June 9, 1910.

Relative Ionizing Energy for the Different Gases.

If we plot the field strengths corresponding to the doubly circled points of Figs. 2 to 18 inclusive as ordinates, and the corresponding pressures as abscissæ, we obtain the straight lines shown in Fig. 19.

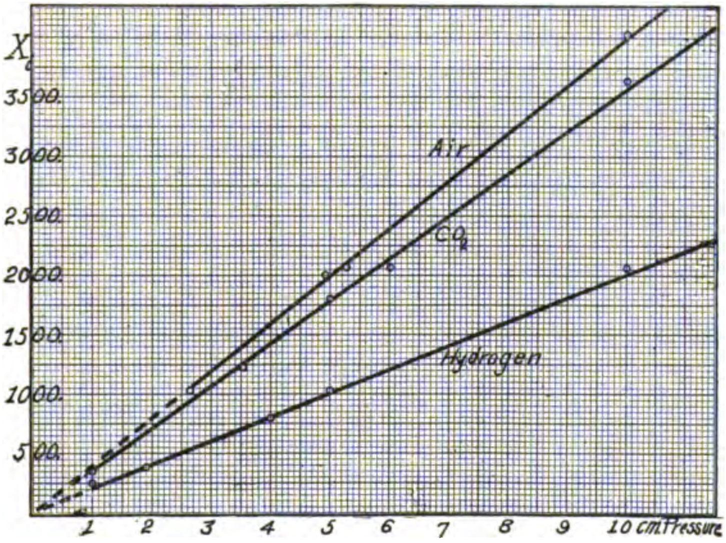

Fig. 11.

These are the minimum ionizing field strengths and are denoted by X_i. From these curves the very important law follows, that the minimum ionizing field strength for any gas is directly proportional to the pressure, or for any gas

$$\frac{X_i}{p} = \text{Cst.} \tag{3}$$

This equation satisfies the conditions at least for pressures above one centimeter. The straight lines are produced as dotted lines back to the origin merely to show that the law is a direct proportion. However, this law, as is well known, does not hold at low pressures and the experimental data would not follow the dotted portions of the curves, but would curve up as very low pressures were approached, the minimum ionizing field strength increasing very rapidly for high vacua. The straight line for hydrogen does not show the results for pressures of 20 and 40 centimeters. The results may be obtained from Figs. 4 and 5, X_i being equal to V/d (volts applied to plate A corresponding to doubly circled points ÷ distance d between the plates). These points fall on the straight line for hydrogen produced. Thus the law X_i/p = Cst has been verified up to 40 cm. pressure for hydrogen, and up to 10 cm. pressure for each of the gases, air and carbon dioxide. This constant was found to be 200 volts per cm. per cm. of pressure for hydrogen, 400 for air,[1] and 356 for carbon dioxide. In obtaining these values the mean of X_i/p for the different pressures was taken, each determination being given a weight proportional to the pressure of the gas.

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[1] Lenard, Drude's Ann. der Phys., Vol. 8, 1902.

[2] O. v. Baeyer, Verhandlungen der Deutschen Physikalischen Gesellschaft, Vol. 10, p. 100, 1908.

First Method—Relative Energy: If the mean free path of the electron were the same in two gases, the relative ionizing energy of these gases would be

$$\frac{E_1}{E_2} = \frac{X_{i_1}}{X_{i_2}}, \tag{4}$$

where E_1 and E_2 are the minimum ionizing energies of the first and second gases respectively, and X_{i_1} and X_{i_2} are the corresponding minimum ionizing field strengths. But the ratio of the mean free paths of the electron in the two gases is the same as the ratio of the mean free paths of the molecules of the two gases, if the electron is negligible in size in comparison to the molecule. Since the energy acquired by the electron between impacts in the two gases is proportional to the mean free paths L_1 and L_2 of the gases, therefore the right hand member of Eq. (4) must be multiplied by this ratio. Hence we have for any two gases

$$\frac{E_1}{E_2} = \frac{X_{i_1}}{X_{i_2}} \cdot \frac{L_1}{L_2}. \tag{5}$$

For air and hydrogen,

$$\frac{E_A}{E_H} = \frac{400}{200} \cdot \frac{.00000983}{.0000185} = 1.063.$$

For air and carbon dioxide,

$$\frac{E_A}{E_{CO_2}} = \frac{400}{356} \cdot \frac{.00000983}{.00000654} = 1.689.$$

---

[1] P. J. Kirkby, Phil. Mag., Feb., 1902, p. 222, states that the smallest value of X/p which gives an appreciable value of α is 40. This corresponds to X/p equal to 400 here since the pressure he used was given in millimeters.

For hydrogen and carbon dioxide,

$$\frac{E_H}{E_{CO_2}} = \frac{200}{356} \cdot \frac{.0000185}{.00000654} = 1.589.$$

Second Method—Relative Energy: The fact that the minimum ionizing energy remains constant at all pressures, taken in connection with the law $X_s/p = \text{Cst}$, shows that the mean free path of the electron in a gas must be inversely proportional to the pressure of the gas. Hence in order to make the mean free path l of the electron the same in two gases, all we have to do is to make the pressures of the two gases proportional to the mean free paths of the gases, *i. e.*, $p_1/p_2 = L_1/L_2$.

If we obtain the ionization curves for these pressures (see Figs. 12 and 13) in the following manner, we shall have the necessary data for determining the relative ionizing energy of the two gases. Accordingly the spark was adjusted so that the value of n_0 was the same in the two gases, *i. e.*, the currents were made the same for the minimum ionizing field strength in each gas. This was done in some cases by changing the intensity of the spark, and in others by adjusting the distance of the spark above the plate.

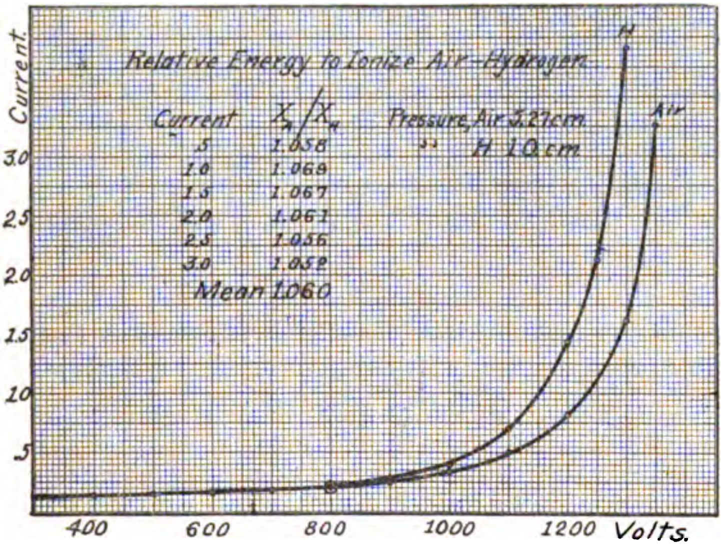

Fig. 12.

Since we have n_0 the same in both gases, it is clear that if we take two points on the two curves where n is the same, *i. e.*, where the ionization currents are equal, then α, the number of ions produced by collision in each gas, must be the same. Having n_0, α, and l the same for both gases their relative energy must be the ratio of the field strengths of any two points on the curves for which n is the same, for since the distance d between the plates was the same for both gases, the relative ionizing energy must be simply the ratio of the positive potentials V, applied to the plate A, or

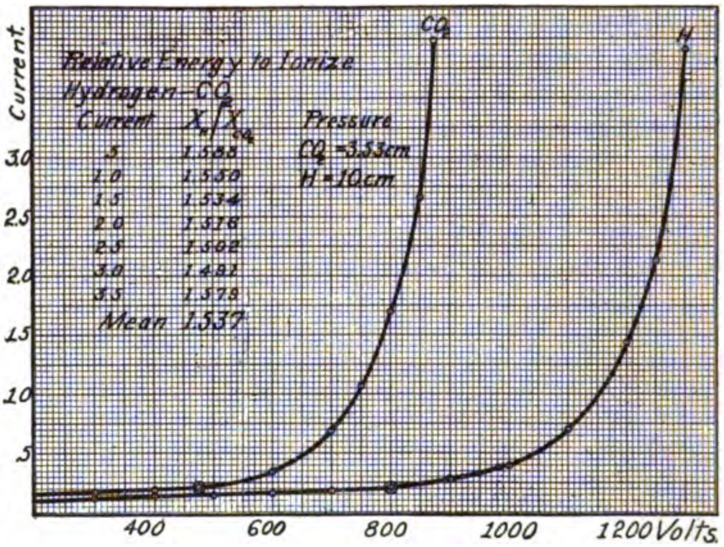

Fig. 13.

$$\frac{E_1}{E_2} = \frac{V_1}{V_2}, \tag{6}$$

when

$$\frac{p_1}{p_2} = \frac{L_1}{L_2}$$

and n_0, α, l, and d are the same for both gases.

For air and hydrogen see Fig. 12 and table accompanying it. Here $E_A/E_H = 1.060$.

For hydrogen and carbon dioxide see Fig. 13 and accompanying table. Here $E_H/E_{CO_2} = 1.537$.

No data were taken by this method for comparing air and carbon dioxide.

Third Method—Relative Energy: A third method for obtaining the relative ionizing energy is by comparing the absolute values given in Table VI. While this is not a direct method, it serves somewhat as a check on the absolute values there given, since it gives the same relative ionizing energy as the first two methods.

For air and hydrogen $\frac{E_A}{E_H} = \frac{10.21}{9.66} = 1.057$.

For air and carbon dioxide, $\frac{E}{E_{CO_2}} = \frac{10.21}{6.21} = 1.644$.

For hydrogen and carbon dioxide, $\frac{E_H}{E_{CO_2}} = \frac{9.66}{6.21} = 1.556$.

For purposes of comparison the results of the three methods are given in Table VII.

TABLE VII.

Relative Ionizing Energies.

	E_A/E_H	E_A/E_{CO_2}	E_H/E_{CO_2}
First method	1.063	1.689	1.589
Second method	1.060	No data.	1.537
Third method	1.057	1.644	1.556

METHOD OF COMPUTING THE FIELD STRENGHTS REQUIRED TO PRODUCE A GIVEN CURRENT IN A PURE GAS.

Professor Townsend has shown that for small values of X/p

$$\frac{\alpha}{p} = F\left(\frac{X}{p}\right), \tag{7}$$

and that when X/p becomes large enough so that the positive as well as the negative ions produce new ones by collision

$$\frac{\beta}{p} = \phi\left(\frac{X}{p}\right), \tag{8}$$

where β is the number of ions (either positive or negative) produced by the collisions of a positive ion in passing through one centimeter of the gas.

In the present work the values of X/p are small compared to those used by Townsend, because of the fact that much higher pressures were used in this work than in his. According to his curves showing the relation between β/p and X/p, the values of β in the present experiments would be entirely negligible. Also since the values of α obtained in these experiments (see Tables I., II., III.) gives a constant value of $X\lambda_0$ for all field strengths and pressures, it follows that in these experiments the positive ions could not have produced new ions by collision.

In order to show that α/p is some function of X/p all of the values of α/p and corresponding values of X/p (taken from Tables I., II., III.), for all of the points observed (see Figs. 2 to 10) were plotted on a large scale, and the result is shown in Fig. 14, which is reduced to about one seventh of the original size. These points fall upon a smooth curve and consequently prove the existence of such a function. When they were plotted it was at once evident that these curves intercepted the X-axis at $X/p = X_i/p$, where X_i/p was the constant determined from Fig. 11

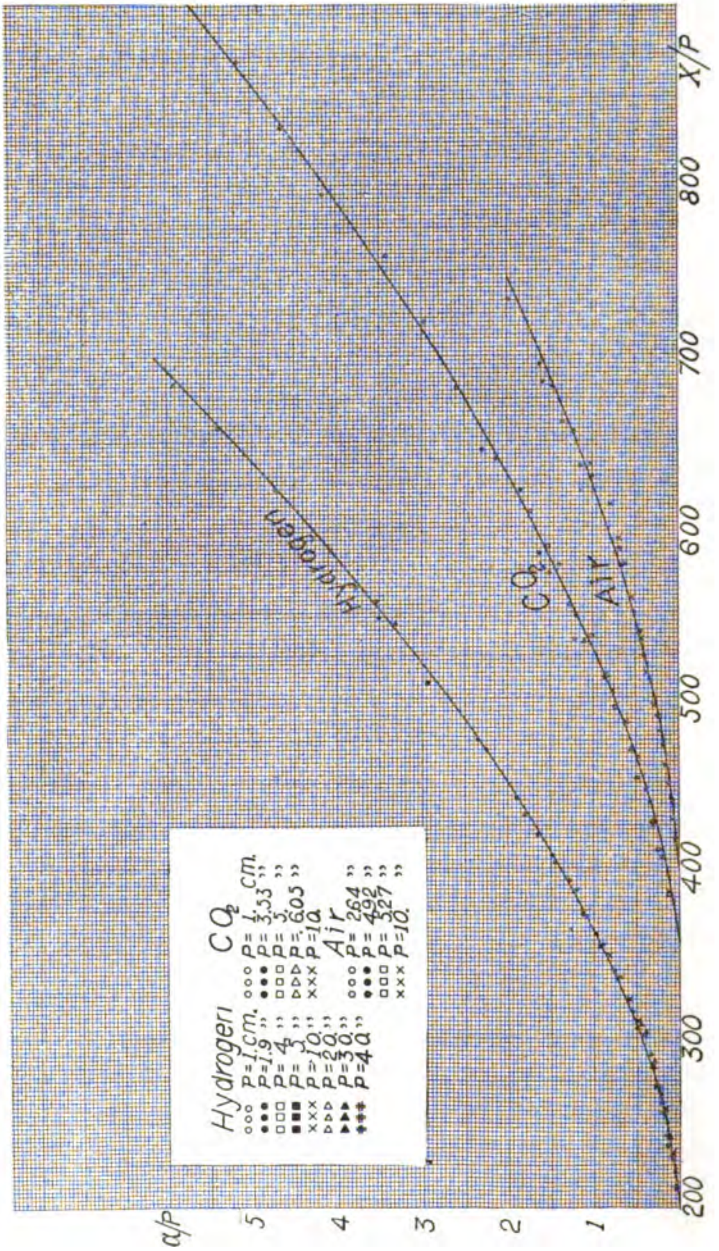

Fig. 14.

for the different gases. This would necessarily have to follow since α must be sensibly zero for field strengths which are very slightly less than the minimum ionizing field strength. Thus the function at once reduces to

$$\frac{\alpha}{p} = f\left(\frac{X}{p} - \frac{X_i}{p}\right), \tag{9}$$

where $X_i/p = 200$ for hydrogen, 356 for carbon dioxide, and 400 for air.

It was then found that all of the curves (Fig. 14) were satisfied by the general equation

$$\frac{\alpha}{p} = a\left(\frac{X}{p} - \frac{X_i}{p}\right)^b, \tag{10}$$

where a and b are constants depending on the gas and were determined from two points which fell exactly on the curve. This gave the following equations for the curves of Fig. 14 for hydrogen, carbon dioxide, and air respectively.

$$\begin{aligned} \frac{\alpha}{p} &= .0002667\left(\frac{X}{p} - 200\right)^{1.615}, \\ \frac{\alpha}{p} &= .0004029\left(\frac{X}{p} - 356\right)^{1.515}, \\ \frac{\alpha}{p} &= .0001594\left(\frac{X}{p} - 400\right)^{1.615}. \end{aligned} \tag{11}$$

From equation (10)

$$\alpha = ap\left(\frac{X}{p} - \frac{X_i}{p}\right)^b.$$

Substituting this value of α in the equation $n = n_0 e^{\alpha d}$ and taking the logarithm of both sides gives

$$\log_e \frac{n}{n_0} = apd\left(\frac{X}{p} - \frac{X_i}{p}\right)^b. \tag{12}$$

This equation with the values of the constants a, b, and X_i/p given in equation (11) was applied to all of the data on pure gases.

The observed values of n/n_0 (see Tables I., II., III.) were substituted in equation (12) and the values of the field strengths X' computed which ought to give that current according to the theory. These computed values of X are given in the fourth column of Tables I., II., III., under the heading X' to distinguish them from the applied field strengths given in the first columns of the same tables under the heading X. The observed and computed values are in nearly all cases within the experimental error, the mean per cent. of difference between them for any gas being less than 1.5 per cent.

APPLICATION TO MIXTURES.

In the following discussion, if we have m per cent. of one gas present in a mixture and $(100 - m)$ per cent. of another gas, we mean by this that the partial pressure of the first is m per cent. of the total pressure of the mixture and that therefore m per cent. of the molecules present are of the first gas and $(100 - m)$ per cent. are molecules of the second gas.

Let Q_1 be the cross section of the first kind of molecules.

Let Q_2 be the cross section of the second kind of molecules.

Let L_1 and L_2 be the mean free paths of the pure gases respectively.

Let the total cross section Q_1 of the first pure gas be represented by 100. Then if we take a mixture of gases containing m per cent. of the first kind and $(100 - m)$ per cent. of the second kind, the total cross section Q_m of the mixture for the same pressure will be

$$Q_m = mQ_1 + (100 - m)Q_2$$

or

$$Q_m = mQ_1 + (100 - m)Q_1\frac{L_1}{L_2}, \tag{13}$$

since from the kinetic theory $Q_1/Q_2 = L_2/L_1$.

Then if the electron is negligibly small and moves with a velocity of order higher than that of the molecules, we may consider the molecules at rest and take the mean free path of the electron in the mixture to be inversely proportional to the cross section Q_m of the mixture. Then if l_1 is the mean free path of the electron in the pure gas and l_m in the mixture we have

$$\frac{l_1}{l_m} = \frac{Q_m}{Q_1}. \tag{14}$$

For hydrogen and air $L_H/L_A = 1.88$. If we let $Q_H = 100$ represent the total cross section of pure hydrogen, Q_{25}, Q_{50}, and Q_{75} represent the total cross sections of mixtures of hydrogen and air containing 25, 50, and 75 per cent. of air respectively, and Q_A the total cross section of air, all for the same pressure, we have, applying equation (13)

$$\begin{aligned} Q_H &= 100, \\ Q_{25} &= 75 + (25 \times 1.88) = 122, \\ Q_{50} &= 50 + (50 \times 1.88) = 144, \\ Q_{75} &= 25 + (75 \times 1.88) = 166, \\ Q_A &= 188. \end{aligned} \tag{15}$$

From the above it is evident that in a mixture of 75 per cent., hydrogen and 25 per cent. air, for example, the mean free path of the electron would be 1.22 times as small in the mixture as in the pure hydrogen at the same pressure. Thus the mean free path of the electron in this mixture is the same as it would be in pure hydrogen at a pressure 1.22 times as great.

In general the electron will behave in ionizing the hydrogen in any mixture as though the pressures were Q_m/Q_H times p where Q_m is the cross section of all the molecules in any mixture and Q_H is the cross section that they would have were they all hydrogen molecules. This new value will be called the apparent pressure and will be denoted by P_1 or

$$P_1 = \frac{Q_m}{Q_H} p. \tag{16}$$

Similarly the electron will behave in ionizing the air in the mixture as though the pressure were

$$P_2 = \frac{Q_m}{Q_A} p. \tag{17}$$

Since there are m per cent. of the hydrogen molecules present at an apparent pressure P_1 and $(100 - m)$ per cent. of the air molecules at an apparent pressure P_2, then equation (12) for a pure gas will become for a mixture of two gases

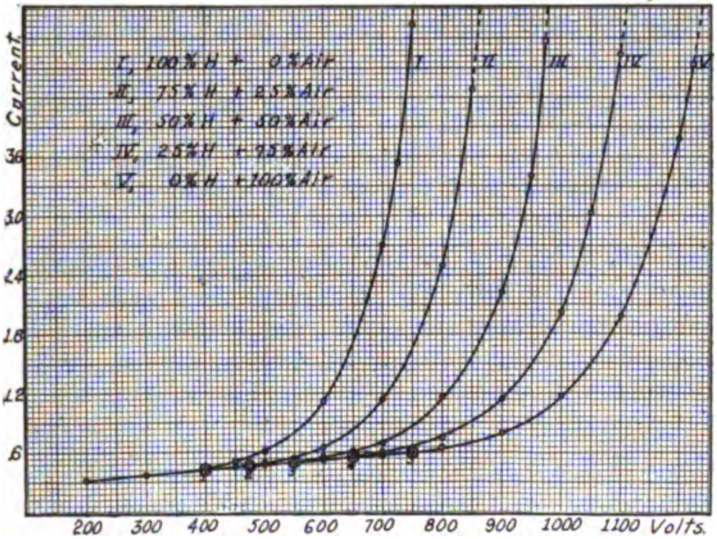

Fig. 15.

$$\log_e \frac{n}{n_0} = m a_1 P_1 d \left(\frac{X}{P_1} - \frac{X_{i_1}}{p}\right)^{b_1} + (100 - m) a_2 P_2 d \left(\frac{X}{P_2} - \frac{X_{i_2}}{p}\right)^{b_2}, \tag{18}$$

where the subscripts refer to the first and second gases respectively. In first term of the right-hand member of equation (18) represents the part of the current due to the ionization of the first gas and the second term that due to the second gas.

For the ionization curves for mixtures of air and hydrogen (See Fig. 15) equation (18) becomes for the different mixtures

$$
\begin{aligned}
&\text{I.}\ \log_e\frac{n}{n_0} = .0002667 \times 5 \times .3875\left(\frac{X}{5} - 200\right)^{1.615}, \\
&\text{II.}\ \log_e\frac{n}{n_0} = .75 \times .0002667 \times 6.1 \times .3875\left(\frac{X}{6.1} - 200\right)^{1.615}, \\
&\qquad + .25 \times .0001594 \times 3.245 \times .3875\left(\frac{X}{3.245} - 400\right)^{1.615}, \\
&\text{III.}\ \log_e\frac{n}{n_0} = .50 \times .0002667 \times 7.2 \times .3875\left(\frac{X}{7.2} - 200\right)^{1.615}, \\
&\qquad + .50 \times .0001594 \times 3.83 \times .3875\left(\frac{X}{3.83} - 400\right)^{1.615}, \\
&\text{IV.}\ \log_e\frac{n}{n_0} = .25 \times .0002667 \times 8.3 \times .3875\left(\frac{X}{8.3} - 200\right)^{1.615}, \\
&\qquad + .75 \times .0001594 \times 4.415 \times .3875\left(\frac{X}{4.415} - 400\right)^{1.615}, \\
&\text{V.}\ \log_e\frac{n}{n_0} = .0001594 \times 5 \times .3875\left(\frac{X}{5} - 400\right)^{1.615}.
\end{aligned}
\tag{19}
$$

To apply the formulæ of (19) the values of the field strengths X' given in the third column of Table VIII. were substituted in the equations and there resulted the values of n/n_0 given in the second column of that table. From the curves (Fig. 15) it was possible to determine what experimental value of X would be required to give the same value of n/n_0, *i. e.*, the same ionization current. These experimental values are given in the first column of Table VIII. headed X. The actual pressure in these mixtures was 5 cm. and the distance between the plates A and B in all cases was .3875 cm. The agreement between the experimental values X and the computed values X' of the field strengths required to produce a given current in the mixtures in all cases was within the experimental error.

It will be noticed that the curves on mixtures of air and hydrogen, II., III., and IV., Fig. 15, are spaced between the curves for the pure gases, I. and V., almost proportionately to the percentage of the mixture. This is what might have been expected since the ionizing energy for air is only six per cent. more than that for hydrogen, so that in mixing the two gases the main effect was to decrease the mean free path of the electron as we increase the content of the air in the mixture, thus increasing the field strength required to produce a given ionization current in approximately the same proportion that the mean free path of the electron has been decreased. The above proportion would be exactly true were the ionizing energies for air and hydrogen the same.

TABLE VIII.

Mixtures of Air and Hydrogen.

I. 100 % H, $n_0 = .420$.			IV. 25 % H, 75 % Air, $n_0 = .548$.		
X	n/n_0	X'	X	n/n_0	X'
1,128	1.15	1,161	1,735	1.03	1,807
1,290	1.44	1,290	2,034	1.34	2,064
1,564	2.77	1,548	2,334	2.13	2,323
1,817	6.68	1,807	2,600	3.92	2,581
1,858	8.18	1,871	2,716	5.57	2,710
1,923	11.10	1,935	2,830	8.16	2,839
II. 75 % H, 25 % Air, $n_0 = .458$.			V. 100 % Air, $n_0 = .600$.		
1,388	1.16	1,419	2,000	1.02	2,064
1,548	1.42	1,548	2,307	1.30	2,323
1,688	1.85	1,677	2,581	1.95	2,581
1,814	2.53	1,807	2,848	3.35	2,839
1,941	3.64	1,935	3,107	6.46	3,097
2,070	5.46	2,064	3,166	7.65	3,161
2,173	8.55	2,194			
III. 50 % H, 50 % Air, $n_0 = 496$.					
1,475	1.03	1,548			
1,798	1.39	1,807			
2,059	2.32	2,064			
2,335	4.60	2,323			
2,452	6.83	2,452			

Consequently it was thought desirable to further test the theory by using mixtures of gases which varied largely in their ionizing energies, and for this purpose mixtures of hydrogen and carbon dioxide were chosen, the ionizing energies of these gases being 1.58×10^{-11} ergs and 1.01×10^{-11} ergs respectively.

APPLICATION TO MIXTURES OF HYDROGEN AND CARBON DIOXIDE.

For hydrogen and carbon dioxide $L_H/L_{CO_2} = 2.83$. If we let $Q_H = 100$ represent the cross section of the hydrogen, Q_{25}, Q_{50}, Q_{75}, represent the cross sections of mixtures of hydrogen and carbon dioxide containing 25, 50, and 75 per cent. of carbon dioxide respectively, and Q_{CO_2} the cross section of the carbon dioxide, then applying equation (13) we have

$$\begin{aligned} Q_H &= 100, \\ Q_{25} &= 75 + (25 \times 2.83) = 145.75, \\ Q_{50} &= 50 + (50 \times 2.83) = 191.5, \\ Q_{75} &= 25 + (75 \times 2.83) = 237.25, \\ Q_{CO_2} &= 283. \end{aligned} \tag{20}$$

If then we apply equations (16) and (17) to those in (20) we shall obtain the apparent pressures for each of the gases hydrogen and carbon dioxide in the mixture. Substituting these values of P_1 and P_2, the values of a_1, a_2, b_1, b_2, from equation (11), the values of m and $(100 - m)$ given in Fig. 16, the values of X_{i_1}/p and X_{i_2}/p for hydrogen and carbon dioxide respectively, and the value of d, all in the general equation (18) and we obtain the following five equations for the curves of Fig. 16.

$$\begin{aligned} \text{I.}\ \log_e \frac{n}{n_0} &= .0002667 \times 5 \times .4\left(\frac{X}{5} - 200\right)^{1.615}, \\ \text{II.}\ \log_e \frac{n}{n_0} &= .75 \times .0002667 \times 7.288 \times .4\left(\frac{X}{7.288} - 200\right)^{1.615}, \\ &\quad + .25 \times .0004029 \times 2.575 \times .4\left(\frac{X}{2.575} - 356\right)^{1.515}, \\ \text{III.}\ \log_e \frac{n}{n_0} &= .50 \times .0002667 \times 9.575 \times .4\left(\frac{X}{9.575} - 200\right)^{1.615}, \\ &\quad + .50 \times .0004029 \times 3.383 \times .4\left(\frac{X}{3.383} - 356\right)^{1.515}, \\ \text{IV.}\ \log_e \frac{n}{n_0} &= .25 \times .0002667 \times 11.86 \times .4\left(\frac{X}{11.86} - 200\right)^{1.615}, \\ &\quad + .75 \times .0004029 \times 4.192 \times .4\left(\frac{X}{4.192} - 356\right)^{1.515}, \\ \text{V.}\ \log_e \frac{n}{n_0} &= .0004029 \times 5 \times .4\left(\frac{X}{5} - 356\right)^{1.515}. \end{aligned} \tag{21}$$

The values of the field strengths given in the last column, Table IX., headed X' were then substituted in the equations of (21) and the corresponding values of n/n_0 computed. Then from the curves of Fig. 16 the experimental values of X which would give the same values of n/n_0 were determined and are given in the first column of Table IX., headed X.

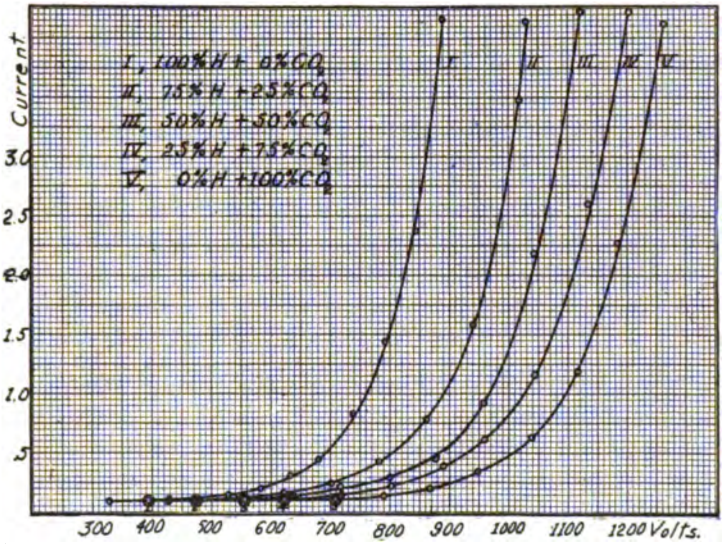

Fig. 16.

TABLE IX.

Mixtures of Hydrogen and Carbon Dioxide.

I. 100% H, $n_0 = .095$.

X	n/n_0	X'
1,512	2.47	1,500
1,730	5.72	1,750
1,875	9.36	1,875
1,995	16	2,000
2,133	28.6	2,125

II 75% H, 25% CO$_2$, $n_0 = .097$.

X	n/n_0	X'
1,600	1.83	1,625
1,720	2.31	1,750
1,990	4.92	2,000
2,272	11.9	2,250
2,530	33.4	2,500

III. 50% H, 50% CO$_2$, $n_0 = .099$.

X	n/n_0	X'
1,737	1.83	1,750
2,000	2.96	2,000
2,265	5.89	2,250
2,490	13.5	2,500
2,765	37.1	2,750

IV. 25% H, 75% CO$_2$ $n_0 = .101$.

X	n/n_0	X'
1,990	2.07	2,000
2,225	3.79	2,250
2,482	7.74	2,500
2,763	19.2	2,750
3,012	42.7	2,950

V. 100% CO$_2$, $n_0 = .103$.

X	n/n_0	X'
2,225	2.20	2,250
2,487	4.49	2,500
2,763	10.5	2,750
3,043	28.0	3,000
3,140	38.6	3,075

The average per cent. of difference between the experimental values X and the computed values X' for the mixtures of hydrogen and carbon dioxide in Table IX. is .9 per cent.; for the mixtures of air and hydrogen in Table VIII. it is also .9 per cent., and for the pure gases, hydrogen, air, and carbon dioxide, in Tables VIII. and IX. it is .9 per cent., 1.5 per cent., and 1.1 per cent., respectively. From this it is seen that the theory has been checked with the same degree of accuracy in mixtures of gases as in pure gases, and that in practically all cases the computed and observed field strengths do not differ by more than the experimental error.

SUMMMARY AND CONCLUSIONS.

1. The theory of ionization by collision has been verified for pressures as high as 40 centimeters.

2. The minimum ionizing energy for any gas is constant, being independent of the pressure and field strength so long as the latter is sufficiently high to produce new ions by collision.

3. These ionizing energies were here found to be 9.66, 6.21, and 10.21 volts, for hydrogen, carbon dioxide, and air, respectively.

4. The minimum ionizing field strength is directly proportional to the pressure, or X_i/p = cst, for pressures at least above one centimeter.

5. The relative ionizing energy of any two gases may be determined by

$$\frac{E_1}{E_2}=\frac{X_{i_1}}{X_{i_2}}\cdot\frac{L_1}{L_2}, \tag{1}$$

where E, X, and L are the ionizing energy, minimum ionizing field strength, and mean free path of the two gases. (2) Or by the second equation

$$\frac{E_1}{E_2}=\frac{V_1}{V_2},$$

where V_1 and V_2 are the potentials applied to plate A, when the pressures of the two gases are in the ratio

$$\frac{p_1}{p_2}=\frac{L_1}{L_2},$$

and n_0, α, l, and d are the same for both gases.

6. The general function

$$\frac{\alpha}{p}=f\left(\frac{X}{p}\right)$$

has been reduced to the special one

$$\frac{\alpha}{p}=a\left(\frac{X}{p}-\frac{X_i}{p}\right)^b.$$

This, combined with the equation $n = n_0 e^{ad}$ gives

$$\log_e \frac{n}{n_0} = apd\left(\frac{X}{p} - \frac{X_i}{p}\right)^b.$$

The second of these equations enables us to determine α for any field strength and pressure, and the third one enables us to compute the field strength required to produce a given value of n/n_0 for any pressure, and distance between plates, within the range of these experiments.

7. By combining the latter expression for two pure gases the value of n/n_0 for any field strength, pressure, and mixture can be computed by a formula of the general form

$$\log_e \frac{n}{n_0} = ma_1P_1d\left(\frac{X}{P_1} - \frac{X_{i_1}}{p}\right)^{b_1} + (100 - m)a_2P_2d\left(\frac{X}{P_2} - \frac{X_{i_2}}{p}\right)^{b_2}.$$

In conclusion the writer wishes to thank Professor Michelson and the staff of the Physics Department for their continued interest in this work, Mr. Fred Pearson for his kind assistance in setting up the apparatus, and especially Professor Millikan for suggesting the problem and for his valuable help and encouragement.

Ryerson Physical Laboratory,
The University of Chicago,
May 2, 1911.

STUDIES IN LUMINESCENCE.

By Edw. L. Nichols and Ernest Merritt.

XVI. The Fluorescence and Absorption of Certain Uranyl Salts.[1]

BECAUSE of their brilliant fluorescence and the interesting character of their absorption spectra the uranyl salts have frequently been the subject of study. The fluorescence spectrum consists of several narrow bands, as many as seven frequently being observable. At low temperatures the bands are so narrow as to be comparable with the bright lines of a gaseous spectrum. Upon observing the spectrum one is struck with the regular arrangement of the bands, which occur with increasing wave-length intervals in passing from violet to red. It would appear that there must be some connection between the bands analogous to that between the different lines of a spectrum series. The absorption spectra of the dissolved salts also consist of a number of sharp and regularly spaced absorption bands, and the absorption spectrum of the solid salts, although less frequently studied, has been found to be of the same general character. It was pointed out by E. Becquerel[2] that the absorption bands appear to form the continuation of the series of fluorescence bands, and in 1885 H. Becquerel[3] found that in the case of uranyl nitrate the two series of bands overlap, so that certain bands may appear either as absorption bands or as luminescence according to the conditions of observation. The same phenomenon has recently been observed with uranyl potassium sulphate at the temperature of liquid hydrogen by J. Becquerel and Onnes.[4]

Our chief purpose in taking up the study of the luminescence of the uranyl salts was to determine whether the different bands of the luminescence spectrum are to be regarded as independent bands, each with its own region of excitation, or whether, as seemed more probable, they form a connected series, such that the excitation of one necessarily involves the excitation of all. In connection with this inquiry we have been led to extend the investigation so as to include other questions connected with the luminescence of these salts, and in the present communication shall describe the results thus far obtained.

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[1] A portion of the apparatus used in this investigation was purchased under a grant from the Carnegie institution.

[2] Mémoires de l'Académie des Sciences, Vol. 40, 1872.

[3] Comptes Rendus, 101, p. 1252, 1885.

[4] Leiden Communications, No. 110, 1909.

WAVE-LENGTHS AND RELATIVE INTENSITIES OF THE BANDS IN THE LUMINESCENCE SPECTRUM.

A list of the salts studied, which were obtained from Kahlbaum, is given in Table I. In each case the wave-length of the crest of each of the fluorescence bands is also given. In measuring these wave-lengths a Hilger constant deviation spectrometer was used. This instrument was provided with two collimators, each having an adjustable slit, and with a Lummer-Brodhun cube; in fact, as constructed for our use it formed a Lummer-Brodhun spectrophotometer, similar in all respects to the usual instrument of this type except for the fact that a constant deviation prism was used. The calibation of the drum was frequently checked by reference to the mercury lines and found to be accurate to within one, or possibly two, Ångström units. The salt was excited by the rays from a quartz mercury lamp, the collimator slit being made as

TABLE I.

Wave-length and Relative Intensity of the Fluorescence Bands.

Uranyl Acetate.		Uranyl Nitrate (Crystals).		Uranyl Nitrate (Anhydrous).		Uranyl Phosphate.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
4,719	1.1	4,708				4,850	
4,875	38.1	4,869	45.2	4,849	43.5	5,015	78.
5,085	100.	5,086	100.	5,071	100.	5,239	100.
5,321	62.1	5,329	50.	5,311	54.	5,483	39.7
5,583	24.3	5,585		5,569		5,748	
5,874	4.2	5,866		5,854			
		6,188		6,145			

Uranyl Sulphate.		Uranyl-potassium Sulphate.		Uranyl Chloride.[1]		Uranyl Fluorid, Fluor Ammonium.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
4,757	2.3	4,766	1.8	4,769		4,843	5.1
4,925	38.	4,920	41.8	4,950		5,008	49.2
(4,891)							
5,149	100.	5,130	100.	5,121		5,237	100.
(5,097)							
5,397	58.8	5,360	65.1	5,369		5,460	57.2
(5,340)							
5,662	21.6	5,606	24.2	5,631		5,727	33.2
5,930	10.9	5,881	9.7	5,928		5,996	16.7
		6,190	2.0			6,294	

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[1] In the case of the chloride the fluorescence was so faint that no attempt was made to determine the relative intensity of the bands.

narrow as the brightness of the luminescence would permit. The crest of each band was located by means of the pointer in the eyepiece, this being set to the position of greatest brightness as estimated by the eye. Owing to the fact that the bands are so narrow no great error can be introduced by this procedure. Upon repeating the settings the different wave-length determinations rarely differed by more than two or three Ångström units, and the variation was usually less than this in the case of the brighter bands. We feel therefore that our wave-length determinations can scarcely be in error by more than five Ångström units and that the accuracy is probably considerably greater than this in the case of bright bands.

In all of the salts studied the general appearance of the luminescence spectrum was much the same, although the bands differed somewhat in width in the case of the different salts. The three principal bands of uranyl nitrate (crystals) are shown in Fig. 1,[1] the excitation being produced in this case by the violet line of the mercury arc at 0.43μ. In the double sulphate of uranyl and potassium (Fig. 2) the bands are much narrower as well as more intense.

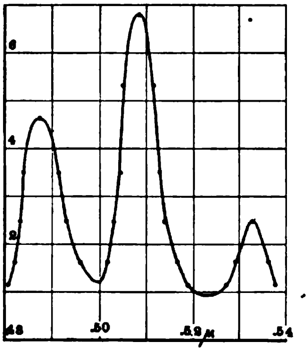

Fig. 1.

The three brightest bands of uranyl nitrate.

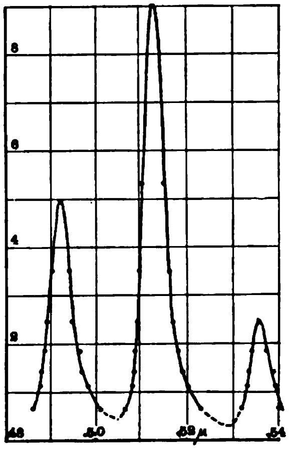

Fig. 2.

The three brightest bands of uranyl-potassium sulphate.

The luminescence spectra of the different salts appeared to differ from one another chiefly as the result of a shift of the spectrum as a whole. In all cases the bands toward the violet end of the series, as well as those lying toward the red, were relatively weak, and the bands of intermediate wave-length were the strongest. Upon measuring the intensities of the different bands in the case of the double sulphate of uranyl and potassium the relative intensities were found to be those indicated graphically in Curve *B*, Fig. 3. Each band is plotted as a line having the wave-length of the crest of the band, and the length of this line is proportional to the measured intensity. The intensity, which was first determined with reference to an acetylene flame, has been expressed in terms of energy, the curve of energy distribution in the acetylene spectrum determined in our previous work[1] being used for this purpose.

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[1] In Figs. 1 and 2 the ordinates show the intensities in the luminescence spectrum as compared with the intensities, for the same wave-lengths, in the spectrum of the acetylene flame.

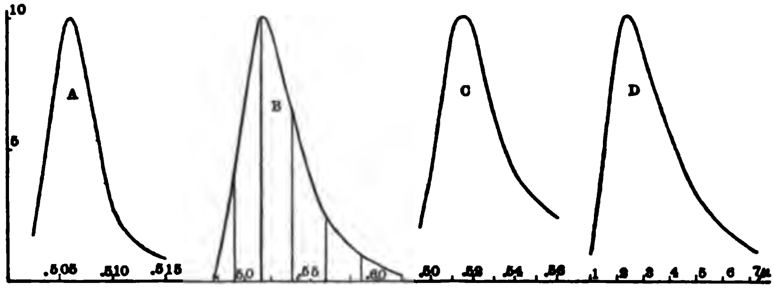

Fig. 3.

A. Energy distribution in the brightest fluorescence band of uranyl-potassium sulphate.

B. Distribution of energy among the seven fluorescence bands of uranyl-potassium sulphate.

C. Energy distribution in the fluorescence band of fluorescein.

D. Energy distribution in the spectrum of a black body at 1259°.

The distribution of energy among the different bands of the series in the case of the uranyl salts seems to be very similar to the distribution of energy in a single band of a luminescent substance like fluorescein, resorufin, or Sidot blende. To bring out this point we have sketched in a curve connecting the upper ends of the lines giving the intensity of the several bands, and for comparison the curve of energy distribution in fluorescein is plotted on the same diagram[2] (Curve *C*).

It is interesting to notice that the distribution of energy in a single band is very similar to the distribution among the several bands. To illustrate this we have plotted as Curve *A*, Fig. 3, the distribution in the brightest band of the double sulphate, the scale of wave-lengths being large as so to make the width of the single band as plotted approximately the same as the width of the groups of bands, *B*. In the same figure we have also plotted for comparison the curve of energy distribution for a black body at 1259° (Curve *D*) the wave-length scale in this case being greatly reduced.[1] It will be noticed that all four curves in Fig. 3 are obviously of the same type.

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[1] PHYSICAL REVIEW, Vol. XXX., p. 328, 1910.

[2] See Nichols and Merritt, PHYSICAL REVIEW, Vol. XXX., p. 328, 1910.

It is known that the width of each of the uranyl bands depends upon the temperature, these bands being almost as narrow as lines at the temperature of liquid air and reaching a width of perhaps 100 Ångström units at ordinary temperatures. It seems probable that at still higher temperatures this broadening would continue and that finally the series of bands would overlap to such an extent as to appear as a single band having somewhat the shape of Curve *B* in Fig. 3. If observations were

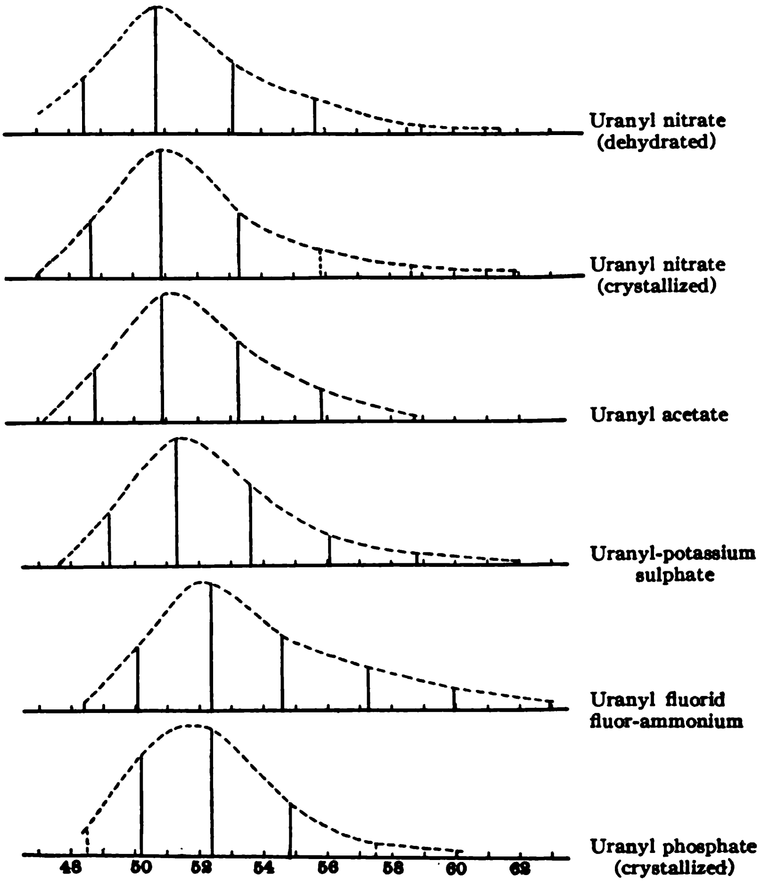

Fig. 4.

Relative intensity of the fluorescence bands of several uranyl salts.

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[1] Plotted from the observations of Lummer and Pringsheim. See Kayser, Handbuch der Spectroscopie, Vol. 2, p. 120.

made at this high temperature only it would not be possible to distinguish the individual bands, and it would be natural to ascribe the luminescence to a single broad band. It appears to us not unlikely that in the case of many luminescent substances the conditions at ordinary temperatures are those which would probably obtain for the uranyl salts at high temperatures, and that the broad luminescence band of a substance like fluorescein is in reality the result of the overlapping of a series of bands. We have indeed recently presented experimental evidence of the complexity of this and other fluorescent compounds.[1]

The relative intensity of the different bands was determined in the case of several salts. The results are presented graphically in Fig. 4 and numerical values are given in Table I.[2] It is clear that the law of distribution of energy among the bands is much the same for all of the salts studied.

The shift in the wave-length of the bands as we pass from one salt to another does not appear to bear any simple relation to the molecular weight of the salt or of its acid component. If we compare, however, the anhydrous and the crystalline nitrate we find that there is a slight shift toward the longer waves in the case of the latter. This seems reasonable on account of the added weight of the water of crystallization.

EXCITATION BY LIGHT OF DIFFERENT WAVE-LENGTHS.

If all the bands of the luminescence spectrum are due to the vibrations of a single connected system it would be natural to expect that an agency which excited one would also excite the rest, especially if luminescence is due to the recombination of ions dissociated by the exciting light, or to the return of an electron set free by the exciting agency. On the other hand if each band is due to some process going on in one particular compound or molecular aggregation it would be natural to expect that wave-lengths might be found which would excite one band and not the rest, or which would at any rate excite the bands in different degree.

To test this matter we have measured the distribution of intensity in the bands for excitation by different lines in the ultraviolet spectrum of the quartz mercury lamp. The intensity of fluorescence with this excitation is not sufficient to permit the measurement of all the bands, so that the three brightest bands only have been measured. In Table II.

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[1] PHYSICAL REVIEW, XXXII., p. 38.

[2] In the case of the nitrate (crystals) and the phosphate the intensity was measured only for the three brightest bands, and the lengths of the dotted lines indicating the intensity of the other bands are estimated. In the case of the anhydrous nitrate the intensity was measured for four bands, but the results for the band at 5,569 were so erratic as to throw doubt on the value of the intensity plotted for this band.

the intensities for excitation by the different lines in the mercury spectrum are given for five different uranyl salts. Curves showing the variation of the relative intensity with the wave-length of the exciting light are shown for uranyl nitrate crystals in Fig. 5, and for the double sulphate in Fig 6. In each case the intensity of the most intense band has been put equal to 10. The variation was greater in the case of the double sulphate than in the case of any other salt studied. The observations were repeated in the case of this substance on two different days and a comparison of the full and dotted curves indicates the extent to which the results agree. In the case of the other salts studied curves very similar to that of Fig. 5 were obtained.

Table II.

Relative Intensity of Excitation of the Three Brightest Bands by Five Different Lines in the Spectrum of the Mercury Arc.

	Wave-length of Exciting Light.	Intensity[1] of Luminescence at Crest of			Ratio *a*/*b*.	Ratio *c*/*b*.
		Band *a*, 4,920 A.U.	Band *b*, 5,130 A.U.	Band *c*, 5,360 A.U.		
Uranyl-potassium	.436μ	12.5	22.7	7.45	0.55	0.33
sulphate.	.407	12.6	26.4	8.45	0.48	0.32
Band *a*.......4,920	.366	10.5	23.2	6.65	0.45	0.29
b.......5,130	.313	16.25	22.9	8.27	0.71	0.36
c.......5,360	.254	8.83	13.9	4.25	0.64	0.31
Uranyl phosphate.	.436μ	10.0	10.2	3.07	0.98	0.30
	.407	6.04	6.06	1.90	1.00	0.31
Band *a*.......5,015	.366	9.7	9.7	2.47	1.00	0.25
b.......5,239	.313	11.1	10.4	3.04	1.07	0.29
c.......5,483	.254	6.85	5.35		1.28	——
Uranyl nitrate	.436μ	22.9	38.7	15.5	0.59	0.41
(anhydrous).	.407	15.3	22.7	9.30	.67	0.41
Band *a*.......4,849	.366	15.3	20.7	8.87	.74	0.43
b.......5,071	.313	21.8	31.6	11.7	.69	0.37
c.......5,311	.254	6.0	7.7	3.2	.78	0.42
Uranyl nitrate	.436μ	18.6	27.2	10.0	0.69	0.37
(crystals).	.407	17.5	24.5	8.6	0.73	0.35
Band *a*.......4,869	.366	12.2	18.3	7.5	0.67	0.41
b.......5,086	.313	17.3	25.6	9.6	0.67	0.38
c.......5,329	.254	8.3	10.5	4.0	0.79	0.38
Uranyl fluorid fluor-	.436μ	10.3	11.2	3.7	0.92	0.33
ammonium.	.407	23.3	25.0	7.7	0.93	0.37
Band *a*.......5,008	.366	20.4	25.7	7.6	0.79	0.30
b.......5,237	.313	37.5	43.4	11.5	0.87	0.27
c.......5,460	.254	15.8	17.6	5.7	0.90	0.32

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[1] The intensities given in Table II. are not corrected for the energy distribution in the acetylene flame.

It will be noticed that the lower curve in Figs. 5 and 6 indicates a very nearly constant ratio between the intensity of the brightest band and that of the band lying next in the direction of the red. But if we compare the brightest band with the band lying next on the violet side we find a considerable variation in the ratio of intensities, especially in the case of the double sulphate. It appears to us probable that this variation is the result of a partial absorption of the luminescence by the substance. The absorbing power of a given salt is probably different for the different mercury lines used, so that in some cases the exciting light may penetrate much further into the substance than in others. It is clear that those bands for which the absorption is greatest will appear relatively weaker when the exciting light penetrates a considerable distance into the substance, even if the relative intensity of the excitation of the different bands is really the same for all wave-lengths of the exciting light. The observed distribution of energy would correspond with the actual distribution only in case an excessively thin layer of the substance is excited,—so thin that the absorption of the light emitted is negligible. As a matter of fact the band lying to the violet side of the maximum is in a region where the absorption is considerable; while the brightest band and those lying to the red are in the region where the absorption is small. The constancy of the ratio in the case of the lower curves, and the small variation of the ratio shown by the upper curves are therefore entirely consistent with the view that the observed variations are the result of absorption, and that the first effect of excitation, whatever may be the wave-length of the exciting light, is to produce all of the bands with a definite and constant intensity distribution.

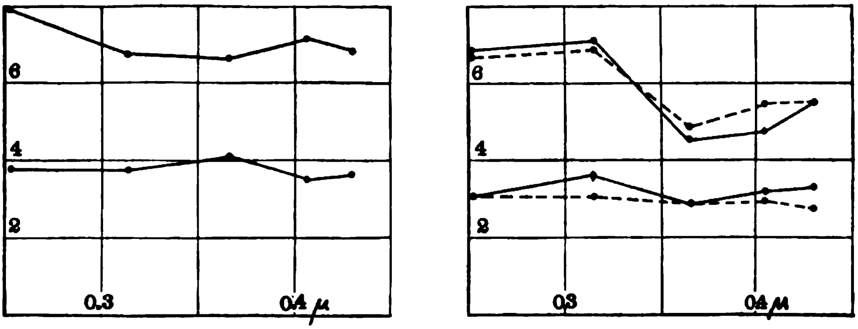

Fig. 5. Fig. 6.

Showing the relative intensities of the brightest fluorescence bands of uranyl nitrate (Fig. 5) and uranyl-potassium sulphate (Fig. 6). The intensity of the brightest band is put equal to 10. The upper curve in each figure refers to the band lying next to the brightest toward the violet. The lower curve refers to the band toward the red. Abscissas give the wave-length of the exciting light. [See Table II.]

ABSORPTION OF THE SOLID SALTS AT ORDINARY TEMPERATURES.

The salts studied by us were in powdered form, none of the crystals being large enough to use for the study of absorption by direct transmission. We have found it possible, however, to determine the location and approximately the relative intensity, of the different absorption bands by measuring with the spectrophotometer the intensity of the light transmitted through an extremely thin layer of the powder held between two plates of glass. Some idea of the character of the absorption spectrum of the salt can also be obtained by observing the spectrum of white light reflected from the surface of the powder, and this method was in some instances used.

The results of measurements of the intensity of the light transmitted by a thin layer of the double sulphate are plotted in Fig. 7, the source of light being an acetylene flame. The measurements cover not only a considerable portion of the absorbing region, but also a part of the region

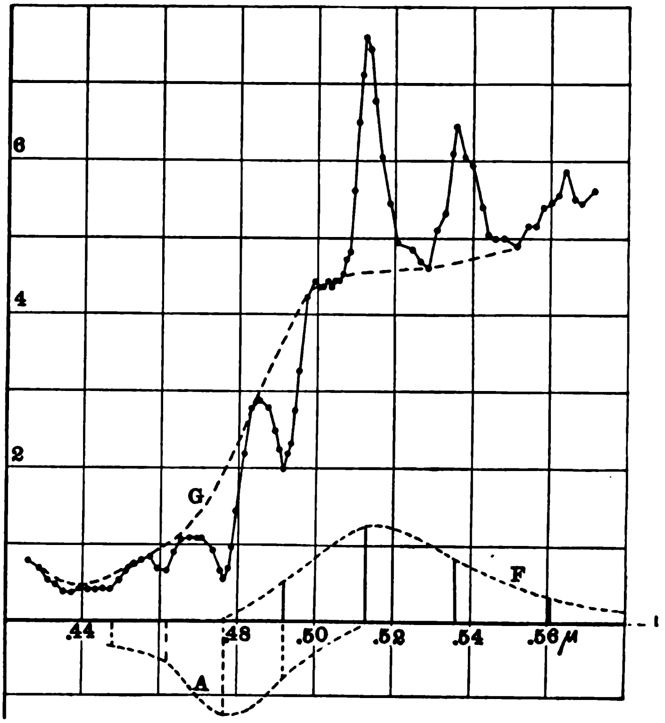

Fig. 7.

Transmission of a thin layer of uranyl-potassium sulphate, showing absorption bands and three of the fluorescence bands. Curves *F* and *A* show the relative intensities of the bands of fluorescence and absorption respectively.

containing the fluorescence bands. Three of these bands show very clearly, even when superposed upon the brilliant continuous spectrum of the acetylene flame. The absorption begins a little on the violet side of the brightest luminescence band and extends to the edge of the visible spectrum. It will be noticed that there are several definite and narrow absorption bands, which appear to be superposed upon a broad band, or region, of general absorption. It is not impossible, however, that this appearance of a broad band results from the overlapping of the group of narrow absorption bands, and that only the crests of these can be observed. There does not appear to be any way of deciding which of these views is correct. In estimating the relative intensity of the absorption bands we have adopted the first view and have assumed a general absorption such as is indicated by the dotted line of Fig. 7. The deviations from this dotted curve have been ascribed to the effect of the narrow bands. The intensity of each band is determined by taking the ratio of the diminution of the transmission which it produces to the transmission which would be expected if the general absorption only were present.

Both the absorption bands and the fluorescence bands have been indicated in Fig. 7 by lines whose lengths are proportional to the intensities of the bands. If a line is drawn through the ends of the lines that give the intensity of the absorption bands a curve (*A*) is obtained which is very similar in form to the absorption curve for a substance like fluorescein. This curve also has the same position with reference to the envelope of the luminescence bands (*F*) that the absorption curve in fluorescein has to the luminescence curve. It appears highly probable that just as a broad luminescence band may result from the overlapping of a group of bands, so the absorption of the same substance may result from the overlapping of a similar group of absorption bands.[1]

The transmission curve for a thin layer of powdered uranyl sulphate is shown in Fig. 8, the source of light being an acetylene flame. In its general features this curve is similar to that for the double sulphate of uranyl and potassium. The fluorescence of the sulphate is not so brilliant and the fluorescence bands therefore show less prominently. The sulphate has the peculiarity of possessing two series of fluorescence bands lying close together, one set of bands being much more intense than the other. It will be noticed that the absorption bands are also double. If we think of the more intense luminescence bands as constituting the principal series and the less intense bands forming a secondary series, a curious reversal is noticeable as we pass from the region of fluorescence to the region of absorption. Each band of the principal series in the luminescence region lies a little to the right of the corresponding band of the secondary series. The positions of the bands are indicated by short vertical lines in the lower part of Fig. 8, the bands of the secondary series being represented by dotted lines. When we pass to the absorption series, however, the more intense band lies to the left in each case. For example, the absorption band at 4,925 corresponds in position with a fluorescence band of the principal series; but the absorption band at 4,880, which probably corresponds to the band 4,890 of the secondary fluorescence series, is by far the more intense of the two.

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[1] If we are mistaken in assuming a broad band of general absorption, upon which narrow bands are superimposed, Curve *A*, Fig. 7, will be shifted to the left and will have its crest at 0.44μ instead of at 0.48μ. But its general form will remain the same.

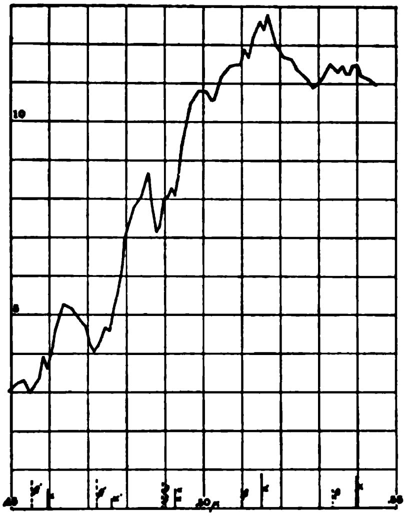

Fig. 8.

Transmission of a thin layer of uranyl sulphate.

It will be observed that the absorption bands of uranyl-potassium sulphate occurring at 4,760 and 4,920 (Fig. 7) appear to coincide in position with two of the luminescence bands of the same substance. In other words these two bands are "reversible" and may appear either as absorption bands or as luminescence bands according to the conditions under which they are observed. The double sulphate thus shows the same phenomenon that was first described by H. Becquerel[1] in 1885 in the case of uranyl nitrate.

The question whether the wave-length of the absorption band is exactly the same as that of the corresponding luminescence band, or whether the agreement is only approximate, is manifestly of great importance, and we have made a number of experiments to test this point. Special precautions were necessary, for when a luminescence band occurs in a region where there is appreciable absorption it is clear that the apparent position of the crest of the band may be influenced by absorption in case the latter is not uniform. Where measurements of absorption are made with light containing rays that are capable of exciting fluorescence there may also be a displacement of the crest of the absorption band owing to the presence of luminescence. There could be no displacement of this sort in case the light emitted were strictly proportional to the coefficient of absorption; but if the fluorescence band and the absorption band do not exactly coincide in position or in form such a displacement is to be expected.

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[1] Comptes Rendus, Vol. 101, p. 1252, 1885.

In order to avoid the necessity of changing the adjustment of the spectrophotometer, or the position of the substance, between measurements a thin layer of the double sulphate was in some cases mounted permanently in front of the slit. To locate the absorption bands the slit was illuminated, through the specimen, with light from an acetylene flame. To observe the luminescence bands a piece of blue glass was placed in front of the flame, so as to cut off the rays having the same wave-length as the bands while permitting the exciting rays to pass; or in some cases the acetylene flame was replaced by a mercury arc. To guard against the presence of fluorescence in measurements of absorption a green glass was sometimes used.

With the relatively thick specimen first used the absorption was so great that the band at 4,760 could not be observed. The band at 4,920 was well defined, however, and could be accurately located. If the eye-piece pointer was set at the crest of the absorption band and the source of light then changed so as to bring out the fluorescence band, the latter was seen to be very obviously displaced toward the red. Photographs of the absorption and fluorescence spectra taken on the same plate also showed the relative displacement of the two bands very clearly. The wave-length of the fluorescence band as measured under these conditions was not the same, however, as that previously determined, and the whole appearance of the band was different from what had been observed when looking at the front surface of the luminescent substance.

More definite conditions for observing the absorption band were obtained by using nearly monochromatic light for transmission measurements. The spectrum of a Nernst glower was formed by a large spectrometer and a small region of the spectrum was isolated by means of a suitable screen containing a slit. The light coming through this slit, after passing through the specimen to be studied, fell upon the slit of the spectrophotometer. By suitable adjustment the center of the band of transmitted light could be made practically coincident with the center of the absorption band and the latter could be located with considerable accuracy. Under these circumstances the transmitted light contained no rays capable of exciting any observable fluorescence, so that we may look upon the determinations of absorption by this method as uninfluenced by errors due to the presence of luminescence.

Using a relatively thick layer the absorption band was located at

4,919, while the crest of the fluorescence band (observed by transmission) lay at 4,974. An excessively thin layer, formed by depositing the salt from a solution, or suspension, in alcohol, gave a fluorescence band whose crest was at 4,925, while the wave-length of the very faint absorption band was 4,922. Our previous determination of the wave-length of the luminescence band, when looking at the surface exposed to the exciting rays, was 4,920. These results appear to us to warrant the conclusion that if disturbances due to absorption could be entirely eliminated the two bands would be found to have exactly the same wave-length.

It must not be forgotten however that it is nearly impossible to observe the fluorescence spectrum under conditions which entirely eliminate effects due to absorption. The exciting light always penetrates to some extent beneath the surface, so that some of the emitted light must pass through the fluorescent material before it can reach the eye. It is natural, therefore, to expect a slight displacement in all cases. Although our most reliable measurement of the wave-length of the absorption band, 4,919, and our best determination of the crest of the luminescence band, 4,920, differ by less than the probable errors of measurement, we feel that it is not unlikely that the difference is a real one, due to the cause just cited.

The absorption band at 4,760 in the double sulphate differs in position by 5 units from the fluorescence band at 4,765. A portion of this difference may also be explained by absorption. But it is probably chiefly due to the difficulty in accurately locating the crests of these bands. The fluorescence band is extremely faint, while the absorption band is not very sharp because of the large general absorption in this region.

Using a thick layer, formed by grinding down a translucent mass of adhering crystals until a piece about 0.5 mm. thick was obtained, a faint absorption band was observed at 5,127. This corresponds to the brilliant fluorescence band at 5,130. In all likelihood the coincidence here is complete, since measurements of the fluorescence band made at the same time and with the same specimen as that used for absorption measurements gave the same wave-length, 5,127, for both bands.

EXCITATION BY LIGHT CORRESPONDING TO DIFFERENT PARTS OF THE ABSORPTION REGION.

It seemed a matter of some interest to determine the relative effectiveness of light of different wave-lengths in producing fluorescence, and experiments having this end in view have been made in the case of the double sulphate. We were particularly interested in determining whether wave-lengths falling within the sharp absorption bands at 4,918, 4,760, 4,615, etc., were especially effective in exciting luminescence.

The source of the exciting light used in these experiments was a Nernst glower which was mounted in place of the slit of a spectrometer. The spectrum was focused upon an opaque screen containing a narrow slit, and the light passing through this slit was used in exciting the specimen tested. The fluorescence spectrum was observed in a spectrophotometer, the specimen being set up at an angle of approximately 45° with the path of the exciting light so that the collimator of the spectrophotometer could be pointed at the illuminated surface without interfering with the exciting light. Enough of the exciting rays were reflected into the spectrophotometer to enable the range of wave-lengths used in each case to be determined. The spectrophotometer was then set at the crest of the principal fluorescence band and the intensity measured by comparison with an acetylene standard. Observations of this sort were repeated throughout the absorbing region. The results are shown in Fig. 9. It will be noticed that the regions of strong excitation at 4,910 and 4,775 correspond very closely to the two absorption bands at 4,920 and 4,766. Some slight indication is also present of the other absorption bands. It is clear, however, that the ability to excite luminescence is not confined to rays falling within the narrow absorption bands, but extends to the region of general absorption lying between. It is not possible to determine the specific exciting power of different rays, as was done in the case of eosin and resorufin,[1] because of our ignorance of the absorbing power of the salt for different wave-lengths.[2] The results indicate, however, that the specific exciting power varies only slightly with the wave-length, as was found to be the case with resorufin and eosin.

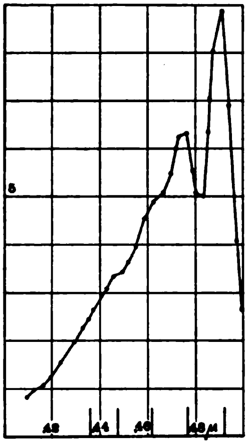

Fig. 9.

Intensity of fluorescence (ordinates) produced by exciting light of different wave-length (abscissas).

Fluorescence and Absorption at Low Temperatures.

To study the fluorescence spectrum at the temperature of liquid air the apparatus described in a previous article of this series[3] and shown in Fig. 10 was used. For excitation we found it preferable to use the undispersed light of a carbon arc. In studying absorption at low temperatures the most convenient procedure was to reflect the light of an acetylene flame from the surface of the powder and compare the reflected light, by means of a spectrophotometer, with light received directly from a similar flame. A curve obtained in this way from the double sulphate of uranyl and potassium is shown in Fig. 11. The region covered includes only two of the absorption bands. In the case of the dotted curve the light from the acetylene flame was first passed through a sheet of green glass, so as to largely remove the rays capable of exciting fluorescence. This was done in order to determine whether the shape and apparent position of the absorption band at 4,894 was influenced by the fluorescence in this region. No shift in the band due to this cause could be detected.

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[1] Physical Review, XXXI., p. 381.

[2] The distribution of energy in the spectrum of the Nernst glower has also not been determined.

[3] Physical Review, XXXII., p. 38.

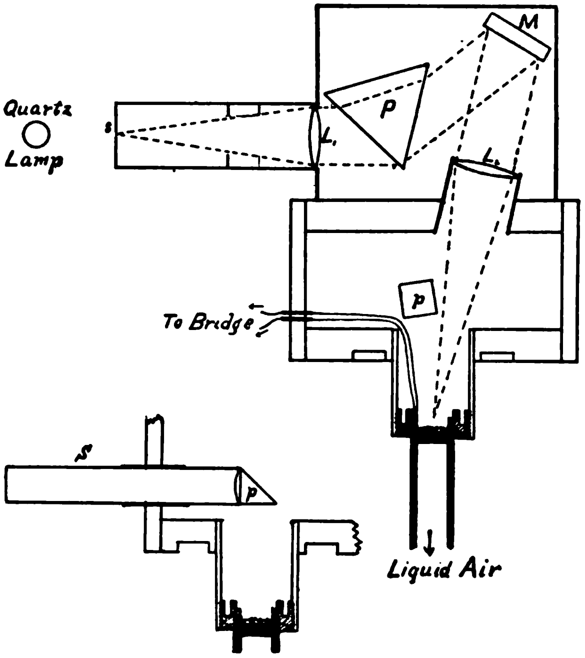

Fig. 10.

At low temperatures the fluorescence bands and the absorption bands appear to be much sharper than at ordinary temperatures. The narrowing of the fluorescence bands is undoubtedly a real effect, since it is verified by photographs of the spectrum and by spectrophotometric measurements. In the case of the absorption bands, however, we are in some doubt whether the narrowing is as great as it appears to be to the eye. If we compare Fig. 11 with Fig. 7, bearing in mind that the horizontal scale is twice as great in Fig. 11 as in Fig. 7, it will be seen that the bands at the temperature of liquid air are not very much narrower than at ordinary temperatures. It must be remembered, however, that the comparison is not quite a fair one, since Fig. 7 is based upon observations of transmission and Fig. 11 on reflection. We do not have any curves that are entirely comparable. Photographs of the transmission spectra, however, at ordinary temperatures and at the temperatures of liquid air fail to show any very marked decrease in the width of the absorption band.

There seems to be no great change in the "general" absorbing power in the violet region as we pass from ordinary temperatures to that of liquid air. To test this matter spectrophotometric measurements of transmission were made with a thin layer of the double sulphate, in powder form, throughout the absorbing region,[1] the measurements being made first at the temperature of the room and then after cooling with liquid air. The results are subject to some uncertainty on account of a slight deposit of frost, but indicate that the general absorption does not change by more than ten or fifteen per cent.

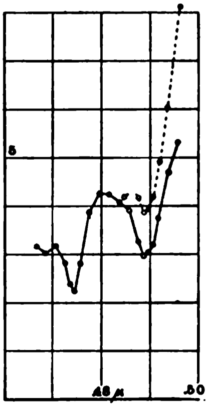

Fig. 11.

Reflection from uranyl-potassium sulphate at − 186° C.

Both the fluorescence bands and the absorption bands show a slight shift in wave-length as the temperature is lowered. At the temperature of liquid air the fluorescence bands of the double sulphate are readily seen to be complex, as has already been pointed out by J. Becquerel. New fluorescence bands, and also new absorption bands, which are not in evidence at all at ordinary temperatures, also become easily observable at the low temperature. The results of determinations of the wave-length of such bands are given in Table V.

Relation between the Absorption and Luminescence Spectra.

In his important memoir on the phosphorescence of the uranium compounds[2] E. Becquerel pointed out in 1872 that the absorption spectrum of each of these substances, like the luminescence spectrum, consists of several regularly spaced narrow bands, and that these absorption bands appear to form a continuation of the series of emission bands in the luminescence spectrum. In 1885 H. Becquerel published wave-length measurements in the case of uranium nitrate,[1] indicating that the increment in wave frequency in passing from one band to the next is constant throughout the series, and that the suggestion of E. Becquerel that the absorption and emission bands belong to the same series is in agreement with the facts, since the frequency difference remains constant in passing from the luminescence to the absorption spectrum. H. Becquerel also showed that two of the bands were reversible; in other words, if the substances were exposed to suitable exciting rays these bands would appear as luminescence bands, whereas if light free from exciting rays was passing through the substance absorption bands would be found in exactly the same location. Reversible bands were also found by H. and J. Becquerel and H. K. Onnes when working with the double phosphate of uranyl and calcium at the temperature of liquid hydrogen.[2] Owing to the sharpness of the bands at this low temperature, and because of the fact that a grating was used, it is probable that the wave-length determinations were considerably more accurate in this work than in any that had preceded it. The photographs show that the absorption and luminescence bands are practically coincident, the difference of wave-length, if it exists, being a fraction of an Ångström unit.

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[1] The observations were made at such wide wave-length intervals that they are of no value in determining the effect of temperature upon the width of the sharp bands.

[2] Memoires del 'Academie des Sciences, Vol. 40, 1872.

TABLE III.

Absorption and Fluorescence Bands of Uranyl-Potassium Sulphate at Ordinary Temperature

Absorption.	Fluorescence.	$n\left(=\frac{3\cdot 10^{10}}{\lambda}\right)$	Δn
4,350		$6,896.4\times 10^{10}$	
			188.1
4,472		6,708.3	
			206.3
4,614		6,502.0	
			206.1
4,760	4,765	6,295.9	
			198.4
4,920	4,920	6,097.5	
			249.5
5,127	5,130	5,848.0	
			251.0
	5,360	5,597.0	
			245.6
	5,606	5,351.4	
			250.2
	5,881	5,101.2	
			254.6
	6,190	4,846.6	

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[1] Comptes Rendus, Vol. 101, p. 1252, 1885.

[2] Leiden Communications, No. 110, 1909.

In our own work with the double sulphate of uranyl and potassium we have confirmed the conclusions of H. Becquerel so far as the existence of reversible bands is concerned and have found in the case of this substance three such bands instead of two. We also find that the increments of wave frequency in passing from one luminescence band to another are very nearly constant. But this increment does not appear to have the same value for the absorption bands as for the luminescence bands, and there is thus a distinct break in the series in passing from luminescence to absorption. This fact is brought out in Table III., which gives the wave-lengths of the bands for uranyl potassium sulphate, together with the wave frequencies and the frequency differences. For the six luminescence bands beginning at 4,920 and ending at 6,190 the frequency differences are very nearly constant, the variation from constancy being not greater than the experimental errors. The series of absorption bands beginning at 4,350 and ending at 4,920 also shows a nearly constant frequency interval. But this differs so greatly from the interval between the luminescence bands that it is hard to believe that the two series of bands belong to the same spectral series.

Table IV.

Fluorescence Bands of Uranyl Sulphate and of Uranyl Acetate.

Sulphate.			**Acetate.**		
λ	**Frequency** $n = 3.10^{10} + \lambda$.	Δn	λ	n	Δn
4,757	$6,306 \times 10^{10}$		4,719	6,357	
		215			203
4,925	6,091		4,875	6,154	
		265			254
5,149	5,826		*5,085*	5,900	
		267			262
5,397	5,559		5,321	5,638	
		261			265
5,662	5,298		5,583	5,373	
		239			266
5,930	5,059		5,874	5,107	

Our results with uranyl sulphate and uranyl acetate, Table IV., are similar in character to those obtained with the double salt. In the case of these salts, however, no absorption bands have been measured. It will be seen that the frequency interval is nearly constant throughout the series of luminescence bands, except between the first two, where the interval is much smaller. If these salts behave like the double sulphate the first three bands are reversible bands and the results are strictly analogous so far as they go to those obtained with the double sulphate.

Owing to the relative broadness of the bands at ordinary temperatures wave-length determinations at these temperatures cannot be very accurate. At lower temperatures, however, the bands become narrow and wave-lengths can be measured much more exactly. Our measurements of the wave-lengths in the case of the double sulphate of uranyl and potassium at the temperature of liquid air are therefore better suited to bring out any numerical relationships that may exist than the observations at ordinary temperatures. The low temperature measurements are given in Table V. As has been pointed out by Becquerel, each of the bands is broken up at the temperature of liquid air into several very narrow bands. The wave-length of each of these has been measured. In several cases the same bands were located by Becquerel and Onnes and their values have also been included in the table. The most intense bands have been indicated by the letter *a*.

TABLE V.

Absorption and Fluorescence Bands of Uranyl-Potassium Sulphate at − 186° *C.*

Absorption.	Fluorescence.	Frequency $n=3.10^{10}\div\lambda$	Δn_a	Fluorescence.	Frequency $n=3.10^{10}\div\lambda$	Δn_a
				(*a*) 5,114.7	5,865×10^{10}	
(*a*) 4,323		6,940×10^{10}		[5,114.8]		
4,437		6,761	221	(*b*) 5,135.5	5,842	
(*a*) 4,465		6,719				251
4,532.5		6,619		(*c*) 5,186.5	5,784	
4,590.5		6,535	196			
(*a*) 4,599.		6,523		(*a*) 5,343.5	5,614	
4,686.5		6,401	205	[5,342.4]		
(*a*) 4,748.5		6,318		(*b*) 5,366.5	5,590	
(*a*) 4,909.	4,907.	6,112	206			
	[4,904.2]			(*c*) 5,418.5	5,537	251
	(*b*) 4,929.5	6,086				
			247	(*a*) 5,593.5	5,363	
	(*c*) 4,974.5	6,031		[5,591.0]		
				(*b*) 5,614.5	5,343	246
	(*a*) 5,114.7	5,865				
	[5,114.8]			(*a*) [5,863.1]	[5,117]	
						239
				(*a*) [6,150]	[4,878]	

The wave-lengths enclosed in brackets are those measured by J. Becquerel and H. Kamerlingh Onnes (Leiden Communications, No. 110, 1909). The band at 6,150 was not observed by us but is recorded by H. Becquerel (Comptes Rendus, Vol. 144, p. 459, 1907).

It will be noticed that the more intense bands form a series with practically constant wave-length interval. The variation from constancy is of importance only in the case of the interval between the last two bands toward the red. One of these was measured by Becquerel and Onnes and the other by H. Becquerel 25 years earlier. Since both lines are faint, and since the apparatus used by H. Becquerel was not capable of great accuracy, it seems probable that the small value of the interval between these two bands is due to some error rather than to a real change in the law.

The five absorption bands which are most prominent also form a series with nearly constant frequency intervals. The absorption band of longest wave-length is a reversible band and corresponds almost exactly in position to the luminescence band of shortest wave-length. There is no reason to suspect that the difference in wave-length of two Ångström units which observations show is anything more than an accidental error.

At the temperature of liquid air we observed only one reversible band, and the luminescence band which at ordinary temperatures was observed at 4,757 was either not present or so faint as to escape observation. The band at 5,114, which is reversible at ordinary temperatures, is in all likelihood reversible at low temperatures. It is necessary at ordinary temperatures to use an especially thick layer of the substance to bring out this extremely faint absorption band and there is no reason to doubt that with proper conditions this band might have been reversed also at low temperatures.

In addition to the principal series, marked (*a*) in the table, there appear to be two other series, whose bands have been marked (*b*) and (*c*) respectively, in which the frequency intervals are also constant. These bands are fainter, however, and only a few can be observed in each series.

While our observations indicate that the frequency intervals between bands are constant within experimental errors, the measurements of Becquerel and Onnes in the case of uranyl salts at low temperatures show a slight tendency for the frequency interval to be smaller at the red end of the series. Although the variation is very slight it is observable in all of the cases studied by them, so that unless some unsuspected systematic error was present it seems that we cannot regard the law of constant frequency increments as being more than a close approximation.

It will be seen that all of our results indicate a distinct break in the spacing of the bands as we pass from the luminescence to the absorption region and thus do not agree with the results of H. Becquerel with uranyl nitrate. It seems to us not unlikely that the measurements upon which Becquerel's conclusions were based were in error. While we have ourselves made no measurements on the absorption spectrum of the nitrate, a large number of absorption bands have been determined for this substance by Jones and Strong[1] and their measurements are not in agreement with those of H. Becquerel. In Table VI. we give the absorption bands as measured by Jones and Strong and the fluorescence bands as measured by ourselves. We have included also the values given by Becquerel in those cases where has he made measurements. In the case of the luminescence bands our wave-length determinations differ from those of Becquerel by more than possible experimental errors in only a few instances. Our determinations are also in close agreement with those of Jones and Strong in the case of the two reversible bands; but the absorption bands at 4,405 and 4,550 (as measured by Jones and Strong) do not correspond at all closely with the bands at 4,370 and 4,530 recorded by Becquerel. If we use the values given by Jones and Strong we find a series of constant frequency intervals throughout the greater portion of the absorption spectrum, but this interval differs by 20 per cent. from the frequency interval that holds throughout the luminescence spectrum.

TABLE VI.

Absorption and Fluorescence Bands of Uranyl Nitrate (cryst.) at Ordinary Temperatures.

Absorption Bands.	Fluorescence Bands.	Frequency $n = 3.10^{10} \div \lambda$.	Δn
3,600		$8,333 \times 10^{10}$	269
(3,720?)		8,064	231
3,830		7,833	210
3,935		7,623	216
4,050		7,407	213
4,170		7,194	177
4,275		7,017	207
4,405 [4,370]		6,810	217
4,550 [4,530]		6,593	221
4,705 [4,700]	4,708 [4,700]	6,372	211
4,870 [4,865]	4,869 [4,865]	6,161	263
	5,086 [5,080]	5,898	268
	5,329 [5,235][2]	5,630	259
	5,585 [5,583]	5,371	257
	5,866 [5,860]	5,114	266
	6,188 [6,180]	4,848	264
	[6,544]	4,584	

In this table the wave-lengths of the absorption bands are those determined by Jones and Strong (American Chemical Journal, Jan., 1910, p. 62).

The wave-lengths enclosed in brackets are those measured by H. Becquerel (Comptes Rendus, 101, p. 1252, 1885).

The wave-lengths of the fluorescence bands are based upon our own measurements.

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[1] American Chemical Journal, Vol. XLII., Jan., 1910.

[2] This appears to be misprint for 5,325.

EFFECT OF WATER OF CRYSTALLIZATION. BEHAVIOR OF SOLUTIONS OF THE URANYL SALTS.

The study of the effect of water of crystallization upon the luminescence and absorption spectra of the uranyl salts, and the comparison of the spectra of the solid compounds with those of their solutions, offer an attractive and important field for further study. Since questions of this kind were aside from the chief purpose of the present investigation we have not gone into them at any length. A few points which have been brought out in the course of our work should, however, be recorded.

The effect of water of crystallization in the case of uranyl nitrate is to shift the luminescence bands slightly in the direction of the longer waves. (See Fig. 4 and Table I.) This is the effect which it would seem most natural to expect, since the mass of the vibrating system is increased by the addition of water of crystallization without any increase, so far as we know, in the elastic forces of the system. In fact the presence of water so intimately associated with the salt molecule would probably increase the effective dielectric constant of the region in which the vibrations occur, and would thus cause a decrease in frequency quite independent of any effect due to increase in mass.

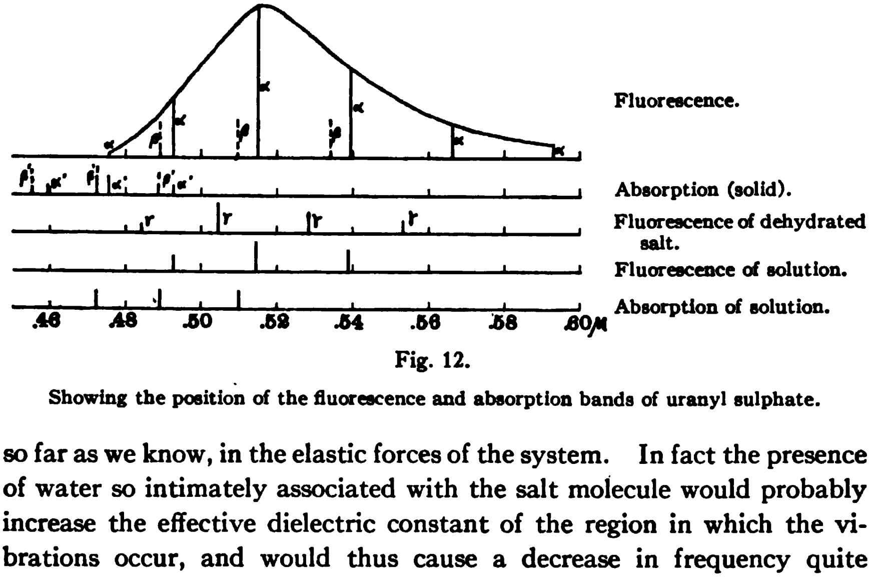

Fig. 12.

Showing the position of the fluorescence and absorption bands of uranyl sulphate.

It has been shown by Deusen[1] and by Jones and Strong[2] that the absorption spectrum of the crystallized nitrate is nearly coincident with the absorption spectrum of the aqueous solution. In many cases no difference can be detected in the wave-length of the band in solution and in the solid crystal. In the case of other bands, however, the difference appears to be too great to be accidental. It seems not unlikely that the absorption spectrum contains several series of bands, some of which occupy almost identically the same positions for the solution as for the solid salt. We must assume therefore that at least a part of the dissolved salt has the same molecular structure as the solid crystals.

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[1] Annalen der Physik, 43, p. 1128, 1898.

[2] American Chemical Journal, Vol. XLIII., p. 37, 1910. See also Vogel, Spectralanalyse, p. 270, 1889.

In the case of the uranyl sulphate studied by us the phenomena are more complicated. The luminescence spectrum of this salt, even at ordinary temperatures, contains two series of bands, which for convenience we shall designate the α and β series respectively. The α bands are by far the stronger and six of these could be observed. Of the relatively weak β bands only three could be seen. In the absorption spectrum of the solid salt two series of bands were also found (see Fig. 8) which we shall call the α' and β' bands. Two of the α' bands corresponded in position with two of the α bands of luminescence, while one band of the β' series corresponded with one of the β bands. The wave-lengths are given in Table VII. and are shown graphically in Fig. 12. It is a remarkable fact that while the α bands are much the brighter in the luminescence spectrum, the α' bands in the absorption spectrum are much weaker than the β' bands.

TABLE VII.

Uranyl Sulphate Fluorescence and Absorption Bands.

Fluorescence.	Crystals—Principal Series (α).....	4763,	4929,	*5148*,	5395,	5659,	5925.
	Crystals—Secondary Series (β)....		4894,	5098,	5340.		
	Dehydrated Salt (γ).............		4843,	*5049*,	5285,	5538.	
	Concentrated Solution...........		4928,	5145,	5387.		
Absorption.	Crystals—α' Series..............	4595,	4755,	4925.			
	Crystals—β' Series..............	4555,	4720,	4880.			
	Concentrated Solution............		4718,	4887,	5095.		

The sulphate as received by us was in the form of small crystals. When the salt was dehydrated by being kept for about an hour in a stream of warm dry air its luminescence spectrum was found to be absolutely different, each band being shifted toward the violet by about 100 Ångström units. Brief exposure to the air apparently permitted a portion of the salt to return to the original condition, so that the original α and β bands could be seen as well as the γ bands characteristic of the dehydrated salt. In the case of a thin layer of the sulphate which had been dehydrated and then exposed for a short time to the air each of the luminescence bands was found to consist of three overlapping bands, the components corresponding in position to the α, β, and γ bands respectively Spectrophotometric measurements (with a rather wide slit) of the brightest luminescence band and of a portion of the absorption spectrum of the same layer are shown in Fig. 13. In the luminescence spectrum the β

bands are by far the most prominent,[1] while in the absorption spectrum the α' bands are strongest and no γ' bands can be detected. The results point to the existence of two different hydrated salts corresponding to the α and β bands respectively. But further study would be necessary to make possible an entirely satisfactory explanation of the observed phenomena.

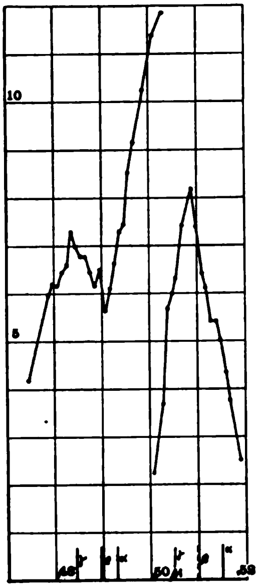

Fig. 13.

Uranyl sulphate (solid). Showing the brightest fluorescence band, at about 0.51μ, and a group of absorption bands, at about 0.49μ.

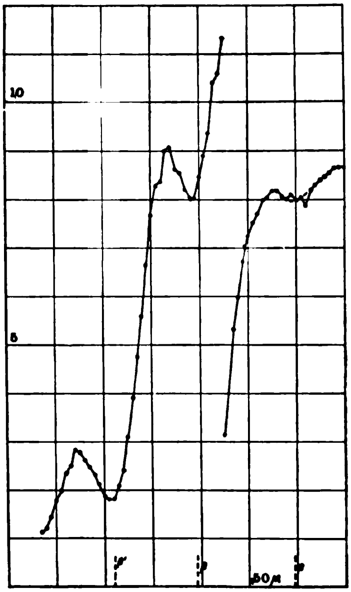

Fig. 14.

Uranyl sulphate (solution) showing at the left a portion of the transmission spectrum for a thin layer, and at the right for a thick layer.

The concentrated aqueous solution of the sulphate showed weak fluorescence, and the three brightest bands, which could be located with reasonable accuracy, were found to agree in position with three of the α bands of the solid crystallized salt. In the absorption spectrum of the concentrated solution it was possible to locate three well-defined bands, two of which corresponded with two of the β bands of the solid salt (see Fig. 14). The solution showed no trace of any fluorescence corresponding to the β series nor did it show any trace of absorption corresponding to the α' series. This peculiar behavior of the solution gives support to the view that the absorption bands of the uranyl compounds do not belong to the same series as the luminescence bands, although they are undoubtedly similar in structure and intimately connected with the luminescence bands.

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[1] The α' band appears in Fig. 13 to be shifted by about 15 Ångström units toward the violet; whether this is a real shift, or whether it is due to disturbances due to simultaneous absorption and luminescence, we are unable to say.

In a concentrated solution of uranyl-potassium sulphate (see Fig. 15) three absorption bands were found at 4,910, 4,730, and 4,570. These do not agree in position with the corresponding bands of the solid salt, which occur at 4,920, 4,760, and 4,472. The solution of the double sulphate shows no trace of fluorescence.

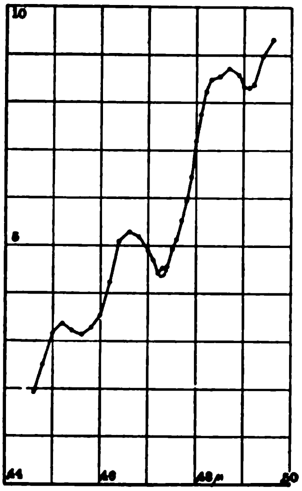

Fig. 15.

Transmission of a concentrated solution of uranyl-pottassium sulphate.

DETERMINATION OF PELTIER ELECTROMOTIVE FORCE FOR SEVERAL METALS BY COMPENSATION METHODS.

By A. E. Caswell.

Introductory Note.—The great discrepancies between the values of the Peltier electromotive force between various metals obtained by different investigators, and especially between the values of Le Roux[1] and Jahn,[2] suggested the advisability of devising a new method of measurement not open to the objections which may be brought against the methods previously employed, and by such method redetermining the Peltier electromotive force for a number of combinations. The development of the thermo-electric and electron theories renders trustworthy determinations of this quantity more important than heretofore. Accordingly, upon the suggestion of Professor Fernando Sanford, the present work was undertaken, and throughout the writer has profited by his timely advice and suggestions as well as that of other members of the department.

Historical Sketch.

Discovery.—Peltier[3] was the first to discover that if a current be sent across the junction of two dissimilar metals there will be either an evolution or absorption of heat at the junction, and if the direction of the current be reversed the effect is also reversed. In other words, the junction of two dissimilar metals is the seat of an electromotive force. Its magnitude cannot be measured directly, so one must resort to the expedient of determining the amount of heat associated with the passage of a given quantity of electricity across the junction, or else deduce its value from more or less doubtful considerations.

Thomson's Theorem.—Through an application of the dynamical theory of heat to thermo-electric phenomena Sir William Thomson (Lord Kelvin) came to the conclusion that, if P = Peltier E.M.F., E = thermo E.M.F., T = absolute temperature, then $P = T\frac{dE}{dT}$.[4] The same considerations led him to the conclusion that a similar effect should exist between unequally heated portions of the same metal. The latter phenomenon was afterward discovered and is known as the Thomson effect. This discovery would seem to verify Thomson's conclusions. If we accept this equation two results follow: (1) knowing the way in in which the thermo E.M.F. varies at any temperature or its value for a very small range of temperature including the desired temperature, we may compute the value of the Peltier E.M.F. for that temperature; and (2) the value of the Peltier E.M.F. at the neutral temperature must be zero. From (1) it follows that at any given temperature the ratio of the Peltier E.M.F. to the thermo E.M.F. for any two metals should be constant and equal to the temperature (absolute). This point has been tested by most experimenters on the Peltier E.M.F. but the results in a number of cases have only been given in relative units. The second result has also been investigated. All the results of experiment seem to justify this equation in a general way.

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[1] Le Roux, Ann. Chim. Phys., IV., 10, pp. 201–291, 1867.

[2] Jahn, Pogg. Ann., N. F., 34, pp. 755–785, 1888.

[3] Peltier, Ann. Chim. Phys., II., 56, pp. 371–386, 1834.

[4] Kelvin, Lord, Math. and Phys. Papers, pp. 232–291, 1882; also Trans. Roy. Soc. Edinburgh, 1854.

Direct Determinations.—The direct determination of the amount of heat associated with the passage of a known quantity of electricity across a metallic junction was carried out by Le Roux who worked with copper against several other metals, notably bismuth. Bismuth bars were welded together into the form of a horse-shoe and to the ends heavy strips of copper were soldered. The junctions were immersed in rather crude calorimeters containing water. Current was sent for fifteen minutes in each direction and corresponding temperature changes in each calorimeter observed by means of mercury thermometers. In the copper-bismuth case the Joule heat was about four times the Peltier heat.

Edlund[1] obtained relative values for the Peltier E.M.F. by means of junctions inclosed in two nickel-plated copper tubes forming the two bulbs of a differential air thermometer. For comparison he also measured the thermo E.M.F. The electromotive force was determined by a sensitive galvanometer and the temperatures by two sensitive mercury thermometers. Assuming that his results for aluminium are the same as those which I have obtained I have computed his values of the Peltier E.M.F. and of the thermo E.M.F. These values are given in the following table. They probably do not differ from his true values by more than ten per cent. The computed values are expressed in millivolts.

Sundell,[2] working with Edlund's apparatus made similar measurements on antimony-bismuth alloys against copper, also on the bismuth used by Edlund. His value for copper-bismuth differed from that obtained by Edlund. This he attributed to some change in the crystalline structure of the bismuth.

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[1] Edlund, Pogg. Ann., *143*, pp. 404–428, and 534–568, 1871; also *140*, pp. 435–450, 1870.

[2] Sundell, Pogg. Ann., *149*, pp. 144–170, 1873.

Jahn determined the Peltier heat by immersing one junction of a couple in a Bunsen ice calorimeter. Current was sent in both directions and the corresponding quantities of heat determined. From these measurements the Peltier heat was calculated. Jahn's results refer to 0° C., and apparently are accurate to within two or three per cent. In order to test the truth of Thomson's theorem Klemenčič measured the thermo E.M.F. of the couples used by Jahn. His results, multiplied by 273, the absolute temperature of Jahn's experiments, together with those of Jahn are shown in Table IX.

Table I.

Edlund's Probable Values.

Metal Used Against Copper.	Peltier E.M.F.		Thermo E.M.F. × 289.	
	Relative.	Computed.	Relative.	Computed.
—				
Iron	130.99	2.96	146.18	3.08
Cadmium	6.88	.155	9.79	.206
Zinc	.34	.008	.76	.016
Copper	——	——	——	——
Silver	1.29	.029	1.89	.040
Gold	14.76	.334	23.92	.505
Lead	22.20	.502	27.27	.575
Tin	24.71	.558	38.84	.82
Aluminium	30.77	.695	42.15	.89
Platinum	45.03	1.017	58.41	1.23
Palladium	96.23	2.175	115.04	2.43
Bismuth	783.1	17.70	835.1	17.62
+				

Cermak,[1] using Lecher's[2] thermo-electric calorimeter, has measured the Peltier effect for couples of constantan against iron, lead, tin, cadmium and mercury, and for a copper-nickel couple, over wide ranges of temperature. His results for the copper-nickel couple are as follows:

Temperatures	19	95	235	290	340	445
Gram-calories $\times 10^3$	1.92	2.15	2.45	2.06	1.01	2.38

The result for 19° C. gives $P = 8.04$ millivolts. He has also found that there is no change either of the Peltier E.M.F. or thermo E.M.F. as the metals change from the solid to the liquid state, or vice versa.

Barker,[3] using the first of the methods employed in the present investigation which he independently devised, has measured the Peltier E.M.F.

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[1] Cermak, Ann. d. Physik, *24*, 2, pp. 351–356, 1907; also *26*, 3, pp. 521–531, 1908. Also in Akad. Wiss. Wien, Sitz. Ber., 116, *2a*, pp. 657–668, 1907.

[2] Lecher, Wiener Ber., 115, *2a*, p. 1506, 1906.

[3] Barker, Phys. Rev., XXXI., p. 321, Oct., 1910.

for a copper-nickel couple and found it to be 6.75 millivolts at 28°.7 C.

The remainder of the work which has been done upon the subject is qualitative rather than quantitative. The values obtained are comparative and cannot be reduced to absolute units. The method used by Peltier himself was to solder two metals bars together in the form of a cross, connect two adjacent extremities to a galvanometer and the other two to a source of current. Current was then sent first in one direction for a given length of time and then in the opposite direction, and the corresponding changes in the galvanometer deflection noted. From these data one might arrange the metals in a Peltier series without giving the actual values of the E.M.F. between any pair. This method has been frequently used. Another common method is to make a thermo-electric couple of the pair of metals to be investigated, and arrange connections so that it may be quickly connected either to a source of current or a galvanometer. Current is sent through the couple thereby heating one junction and cooling the other. The circuit is then broken and the couple connected with the galvanometer. The galvanometer deflection may be used to compute the difference in temperature. For a given current this difference should be approximately proportional to the Peltier E.M.F.

Lenz[1] bored a small hole in the junction of two coaxial bars of bismuth and antimony. This he filled with water and cooled the whole apparatus to 0° C. Then by sending a current across the junction from bismuth to antimony he was able, not only to freeze the water in the hole, but also, to cool the ice to − 4°.5 C.

Proportional to Current.—Icilius,[2] using a thermopile consisting of 32 bismuth-antimony couples, found that the heating or cooling of the junctions was proportional to the strength of the current sent across them. Frankenheim[3] confirmed this result by using Peltier crosses of bismuth-copper, copper-iron, bismuth-antimony, and iron-German-silver.

Zero at the Neutral Point.—Budde[4] investigated the question regarding the value of the Peltier effect at the thermo-electric neutral point for copper-iron and zinc-silver couples. In the latter case the thermo E.M.F. was too small for him to get any satisfactory results. Using the second of the qualitative methods mentioned above he found the Peltier effect to be zero at 240° C. and the thermo E.M.F. zero at 270° C. for the copper-iron couple. This he considered a sufficient agreement. In a similar way Battelli[1] investigated the Peltier effect and thermo E.M.F. for lead against (1) an alloy of 10 parts antimony to 1 part tin, and (2) an alloy of 18 parts tin to 1 part cadmium. For the thermo E.M.F. he found the neutral points to be 12° C. and 16° C., respectively. The Peltier effect was zero at 16° C. and 31°.5 C. Believing that the experiments of Budde and Battelli by no means prove that the Peltier effect is zero at the neutral point, La Rosa[2] investigated the point very carefully. To the ends of a bar of pure zinc bent into the form of a V, he soldered iron and platinum wires. The iron wires were connected to the galvanometer, and current sent through the platinum-zinc junctions. Readings were taken from 19° C. to 46°.5 C., the neutral point being found at 36°.6 C. The curve for temperatures as abscissæ and galvanometer deflections as ordinates cut the temperature axis slightly above 36°.5 C. Therefore the Peltier effect becomes zero at the neutral point within the limits of experimental error.

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[1] Lenz, Pogg. Ann., *44*, p. 342, 1838.

[2] Icilius, Pogg. Ann., *89*, p. 377, 1853.

[3] Frankenheim, Pogg. Ann., *91*, p. 161, 1854.

[4] Budde, Pogg. Ann., *153*, pp. 343–372, 1874.

Agreement with Thermo-electric Diagram.—Campbell,[3] using couples consisting of a U-shaped piece of lead or other metal soldered to iron blocks, obtained results which appear to agree with the thermo-electric diagram given in Tait's manual on "Heat." The temperature differences of his junctions were measured by means of an iron-German-silver thermo-couple, separated from the junctions by several thicknesses of paper. Gore[4] obtained similar results using a thermopile, consisting of 36 bismuth-antimony couples, heated in a hot-water jacketed chamber from 9° to 85° C. With Peltier crosses he also found that the Peltier effect increased with temperature for iron-German-silver, bismuth-antimony, and bismuth-silver. For antimony-silver it seemed constant.

Variation with Temperature.—By means of Thomson's equation, $P = T\frac{dE}{dT}$, Harrison[5] has found the value of the Peltier E.M.F. at the temperature of liquid air (− 191°.2 C.). His results are:

Copper-iron	1,156 microvolts,
Copper-nickel	7,697 microvolts.

Bausenwein[6] has found that, for the iron-constantan couple which he used, both the thermo E.M.F. and the Peltier E.M.F. increase in a linear manner with the temperature (absolute). But the Peltier effect is not proportional to the absolute temperature, its curve cutting the axis of temperatures at −600° C. Hence this combination does not obey Thomson's law. His experiments extended over the interval from 0° C. to 800° C. Rzika[1] carried out similar measurements on a couple made from the same metals and obtained contradictory results. The principal source of error is probably due to changes in the specific heats at high temperatures, which changes are not known. The question of variation with temperature is still unsettled.

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[1] Battelli, R. Acc. dei Lincei (1) Rendic., *3*, pp. 404–407, 1887, also Beibl., *11*, 726, 1887.

[2] LaRosa, Acc. Lincei, Atti, *13*, pp. 167–173, 1904; also Sc. Abs., 7, 2968.

[3] Campbell, Proc. Roy. Soc. Edinburgh, *11*, 807, 1882–3; also Beibl., *8*, p. 231, 1884.

[4] Gore, Phil. Mag. 3, *21*, pp. 351–362, 1886.

[5] Harrison, Phil. Mag., 6, *3*, pp. 177–195, 1902.

[6] Bausenwein, Akad. Wiss. Wien, Sitz. Ber., *144*, *2a*, pp. 1625–1633, 1905; also Sc. Abs., *9*, 1110.

Theories.—In addition to Sir William Thomson's theoretical work on thermo-electricity, two recent developments are of interest. The first is the explanation of the Peltier effect upon the basis of the electron theory,[2] the second is due to Lecher.[3]

Electron Theory.—In the electron theory it is assumed that the concentration of the electrons in any two metals is, in general, different for the same temperature. If, then, two metals are placed in contact, the electrons will diffuse from that metal in which the concentration is large to that in which it is small. This diffusion will continue until the electric field set up by the motion of the electrons away from their compensating positive charges is sufficient to balance the difference of pressure due to the difference of concentration. The resulting potential difference, assumed to be identical with the Peltier E.M.F., is given by the equation $P = \frac{4\alpha T}{3\epsilon} \log \frac{N_1}{N_2}$, where N_1, N_2 are the concentrations of the electrons in the two metals, αT is the mean kinetic energy of an electron, and ϵ is the charge on an electron. From other considerations N is found to be proportional to the inverse of the square root of the absolute temperature. Hence N_1/N_2 is constant. The Peltier E.M.F. should, therefore, be strictly proportional to the absolute temperature, and so could not be zero at the neutral point unless it were zero at all temperatures. This seems to be contrary to the facts.

Lecher's Diagram—Lecher obtains the Peltier heat by superimposing upon a diagram representing the Thomson heat for the two metals concerned, a curve representing the energy of the thermo E.M.F. between the two metals. In this way he finds the Peltier effect between iron and silver to be 7.3 × 10^{-4} gram-calories per coulomb, or 3.06 millivolts. This agrees well with experiment as may be seen by referring to Table IX.

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[1] Rzika, Akad. Wiss. Wien, Sitz. Ber., *116*, *2a*, pp. 715–722, 1907; also Science Abs., *11*, 26.

[2] Drude, Ann. d. Physik, 4, *1*, p. 566, 1900, and 4, *3*, p. 369, 1900.

[3] Lecher, Ann. d. Physik, 4, *20*, pp. 480–502, 1906.

METHODS OF MEASUREMENT.

Two methods of measurement were devised, both of which depend upon maintaining both junctions of the given couple at the same temperature by supplying heat at the junction where cooling is taking place. This precludes the possibility of error arising out of other thermo-electric effects. The Peltier electromotive force is determined by measuring the ratio of the heat so supplied to the quantity of electricity sent across the junction. The first method, as previously stated, has also been devised by Barker and by him employed in the measurement of the Peltier E.M.F. in a copper-nickel junction. In view of the fact that measurements were already being made by this method when his article was published, also that he had not investigated the method completely and intimated that he had discontinued the work, it was decided to proceed. The discussion of the method and the mathematical calculations here given are fuller than those in his article, and so may justify such repetitions as occur.

FIRST, OR SEPARATE HEATING-COIL, METHOD.

This consists essentially in placing the two junctions of the couple in two separate calorimeters containing equal quantities of a suitable liquid. Each is provided with an electric heating-coil of known resistance, by means of which sufficient heat is supplied to the liquid where cooling is taking place to maintain it at the same temperature as that where heat is evolved, the equality of temperature being shown by a differential thermometer.

Two Dewar silvered glass vacuum flasks (inside dimensions: diameter 3.1 cm., depth 15 cm.) were used as calorimeters because they are the best heat insulators available and their heat capacity is small. These were held upright in a wooden box. The couples were made from heavy strips of the metals and were in the form of a double U, the junctions being at the bottoms of the U's.

Apparatus.—Three different forms of heating-coil were tried. The first coils, used only with the gas stirrers mentioned below, consisted of a considerable length of manganin wire doubled and then kinked as shown in Fig. 1. These were placed in the center of the U and extended upward to the surface of the liquid. This form was discarded because the coils occupied too much space. Coils of 65 cm. of German-silver resistance wire were then made. The wire was wound around a celluloid hoop, the perimeter of which was 6.5 cm. and depth 2.5 cm. The manner of winding is shown in Fig. 2. The hoop was placed in the center of the U with its axis vertical, and the stirrer and one junction of the thermo-element, used as a thermometer, were placed within it. The resistance of these coils was 3.057 and 3.072 ohms, respectively. This arrangement was abandoned because the hoop, by impeding the circulation of the liquid, lengthened the time elapsing before a steady temperature condition could be set up. The arrangement finally adopted was similar to the first except that the wire was crowded into small space and placed in the bottom of the U as shown in Fig. 3. The length of the coils so formed was 2.5 cm., so that they extended across the calorimeters. In this way heat was supplied very close to the place where it was being absorbed, and the coil, while being small, permitted free circulation of the liquid. Two sets were made in this way. They were of German-silver wire similar to that used in the "hoop" coils. The resistance of the first set was 4.503 and 4.509 ohms, and of the second set 1.490 and 1.505 ohms.

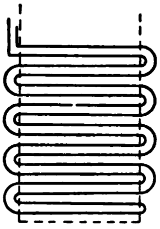

Fig. 1.

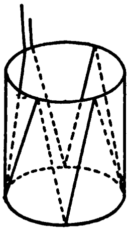

Fig. 2.

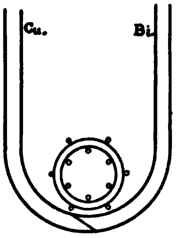

Fig. 3.

In the preliminary experiments instead of a differential thermometer two mercury thermometers, graduated to tenths of a degree Centigrade and readable to hundredths, were used. These were read as nearly simultaneously as possible. Owing to their comparatively great bulk, mercury thermometers are not suitable, and so were replaced as soon as possible by a differential thermometer consisting of four copper-constantan thermo-elements in series. No. 24 constantan and No. 26 copper wire were used. The resistance of the set was about 4.5 ohms. These were connected to a sensitive Siemens and Halske D'Arsonval galvanometer of 91.6 ohms resistance, the deflections being observed by means of a powerful reading telescope to which a glass scale was attached, the distance from mirror to scale being 150 cm. A deflection of 9.2 cm. corresponded to a temperature difference of 0°.1 C. The scale could be easily read to 0.01 cm. The sensitiveness of the apparatus varied to a certain extent because of the quantity of liquid not being always the same, and because the heat capacity of the immersed metal also differed for the different junctions. An idea of the sensitiveness may be gained from the fact that in the case of the copper-silver junction (see section on copper-silver) a reversal of the heating effect of a current of 0.036 ampere through a coil of 4.5 ohms resistance produced a change of 0.27 cm. per minute in the rate of deflection of the galvanometer. That is, the addition of 2.59 joules of heat (0.62 calories) to one calorimeter would change the deflection of the galvanometer one centimeter. In the case of copper-platinum the addition of 2.18 joules was sufficient to change the deflection of the galvanometer one centimeter.

The stirring of the liquid was first attempted by means of gas stirrers. Each of these consisted simply of a capillary glass tube, one end of which was placed in the bottom of the calorimeter, the other being connected to a tank containing air under a slight pressure. These were used only with the mercury thermometers. It was found that whenever a bubble of air happened to strike the thermometer the latter tended to give the temperature of the air rather than that of the liquid, in consequence rotary stirrers were substituted in the later experiments. These consisted of semi-circular disks of copper, 0.4 cm. radius, soldered to steel knitting-needles. Each was supported and made adjustable by means of two bearings, one at the top of the calorimeter, the other about 7 cm. above it. The stirrers were driven by a small electric motor.

The openings of the calorimeters were partially closed either by cork stoppers, as in the case of copper-silver, or by pieces of cloth laid over the tops of the calorimeters. It was found that when the calorimeters were not shielded in any way the unequal lighting of the room had an appreciable effect upon the amount of heat required by each calorimeter, and in consequence the whole apparatus was surrounded by a box provided with a heating-coil, by means of which, with the aid of a thermostat, the air could be kept at a constant temperature. As will be seen later, it is not important that there should be no heat lost by the calorimeters, but that this loss should be as nearly as possible the same for both. This and other vitiating effects will be discussed under the head of probable sources of error.

Throughout the experiments kerosene was used as the calorimetric fluid, being chosen on account of its mobility and low specific heat. Equal amounts were measured into the calorimeters by means of a pipette. From 35 to 40 c.c. was used in each calorimeter.

In order to be able to determine the temperature difference of the metallic junctions during an experiment when the temperature of the liquid was the same in both calorimeters, they were connected to the galvanometer by means of a double-throw switch so that they could replace the thermo-elements. By determining their thermo E.M.F. by comparison, the temperature difference could be computed. This measurement must necessarily be made *after* the current through the junctions is stopped, and in consequence the deflection obtained is less than it should be owing to communication of heat to the liquid.

The approximate temperatures of the experiments were obtained by inserting a mercury thermometer into one of the calorimeters before and after a run and reading the temperature.

Currents were measured by means of Siemens and Halske milliammeters with suitable shunts. The compensating current was supplied by a single storage cell, while the main current was supplied by storage batteries of 4, 6, or 8 storage cells in series, or two sets of 8 cells in series in parallel, depending upon circumstances. The single cell supplied a perfectly uniform current, but the batteries frequently varied as much as one per cent., and occasionally as much as two or three per cent. These variations will not affect the final result materially since the current was read at regular intervals of one or two minutes each.

A sectional view of the calorimeters is shown in Fig. 4, while all the electrical connections are shown diagrammatically in Fig. 5.

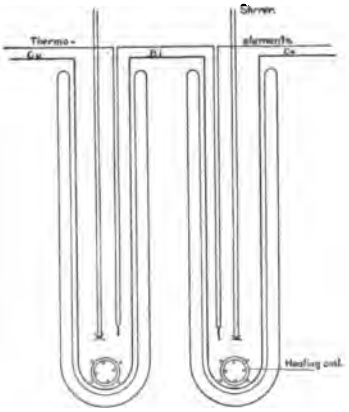

Fig. 4.

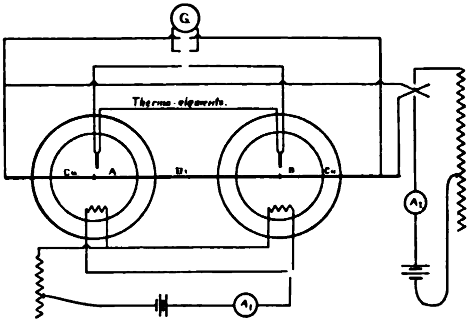

Fig. 5.

Mathematical Discussion.—The following mathematical discussion is somewhat more complete than that given by Barker, to which reference has already been made. If we denote the two calorimeters as A and B, and for the quantities corresponding to each use the subscripts a and b, respectively, we may use symbols for the quantities involved as follows:

P = Peltier E.M.F. expressed in volts,

r = resistance of compensating heating-coil in ohms,

R = effective resistance of junction,

i = compensating current in amperes,

I = main current through the junctions,

C = heat capacity of calorimeter and contents *expressed in joules*,

h = rate of heat loss to surrounding bodies dependent upon a difference in temperature of 1° Centigrade,

θ = temperature of liquid minus temperature of surrounding bodies,

s = heat gained from external sources independent of any temperature differences (*i. e.*, through stirring, etc.).

Case I.—When direction of the current is such that heat is absorbed in A, and evolved in B, we have

$$\frac{I_a^2R_a - PI_a + i_a^2r_a - h_a\theta_a + s_a}{C_a} = \frac{I_a^2R_b + PI_a - h_b\theta_a + s_b}{C_b},$$

or

$$C_a(I_a^2R_b + PI_a - h_b\theta_a + s_b) = C_b(I_a^2R_a - PI_u + i_a^2r_a - h_a\theta_a + s_a),$$

or

$$PI_a(C_a + C_b) = I_a^2(C_bR_a - C_aR_b) - \theta_a(C_bh_a - C_ah_b) + C_bi_a^2r_a + (C_bs_a - C_as_b),$$

whence

$$P = \frac{I_a(C_bR_a - C_aR_b)}{(C_a + C_b)} + \frac{C_bi_a^2r_a}{I_a(C_a + C_b)} - \frac{\theta_a(C_bh_a - C_ah_b)}{I_a(C_a + C_b)} + \frac{C_bs_a - C_as_b}{I_a(C_a + C_b)}. \tag{1}$$

Case II.—In a similar way we may obtain the following equation for the case when the current is reversed.

$$P = \frac{I_b(C_aR_b - C_bR_a)}{C_a + C_b} + \frac{C_ai_b^2r_b}{I_b(C_a + C_b)} - \frac{\theta_b(C_ah_b - C_bh_a)}{I_b(C_a + C_b)} + \frac{C_as_b - C_bs_a}{I_b(C_a + C_b)}. \tag{2}$$

Adding equations (1) and (2) we obtain

$$P = \frac{1}{2}\left[\frac{I_a - I_b}{C_a + C_b}(C_bR_a - C_aR_b) + \frac{1}{C_a + C_b}\left(\frac{C_bi_a^2r_a}{I_a} + \frac{C_ai_b^2r_b}{I_b}\right) - \frac{\frac{\theta_a}{I_a} - \frac{\theta_b}{I_b}}{C_a + C_b}(C_bh_a - C_ah_b) - \frac{\frac{1}{I_a} - \frac{1}{I_b}}{C_a + C_b}(C_bs_a - C_as_b)\right]. \tag{3}$$

If $I_a = I_b$, the first and fourth terms on the right-hand side of the equation vanish. This condition is easily realized. If, in addition, $C_a = C_b$, the second becomes $+\dfrac{i_a^2r_a + i_b^2r_b}{4I}$, and the third term becomes

$-\dfrac{\theta_a - \theta_b}{4I}(h_a - h_b)$. Since θ_a and θ_b are both small and approximately equal, the same being supposed to be true of h_a and h_b, the last term may be neglected without any great error. We have then simply

$$P = \frac{i_a^2 r_a + i_b^2 r_b}{4I}. \tag{4}$$

This equation is the one used in all the numerical computations. It depends as we have seen upon the assumption that $C_a = C_b$. This condition may not be very fully realized so it is advisable to consider equation (3) a little farther. Considering only the second and third terms, let us suppose that $C_a + c = C_b$, where c is small in comparison with C_a. Then

$$P = \frac{1}{2I(2C_a + c)}[C_a\{i_a^2 r_a + i_b^2 r_b - (\theta_a - \theta_b)(h_a - h_b)\} \\ + c\{i_a^2 r_a - h_a(\theta_a - \theta_b)\}].$$

If we expand $\dfrac{1}{2C_a + c}$ by the binomial theorem and sum the resultant product as two geometrical progressions we obtain

$$P = \frac{1}{4I}[i_a^2 r_a + i_b^2 r_b - (\theta_a - \theta_b)(h_a - h_b) \\ + \frac{c}{2C_a + c}\{i_a^2 r_a - i_b^2 r_b - (\theta_a - \theta_b)(h_a + h_b)\}]. \tag{5}$$

Obviously a small difference in the heat capacities of the calorimetric systems will have but little effect upon the final result, unless perchance h_a and h_b should be quite large, which is improbable.

Probable Advantages of Method.—Practically all the methods hitherto employed in the measurement of the Peltier E.M.F. involve temperature differences between the junctions which must necessarily involve both the Thomson and Seebeck effects. It is impossible to say with certainty what effect these phenomena will have upon the resulting value obtained for the Peltier E.M.F. These disturbing effects are effectually eliminated by the present method. This is shown by the temperature differences found for the junctions. Errors due to loss of heat to surrounding bodies, etc., are reduced to a minimum since the other methods used do not take account of it, and it must have been quite large in some cases. In other cases it is doubtful whether the temperature differences, or other quantities, measured to determine the amount of heat involved, really were the temperature differences required. This would be due to a non-uniform distribution of heat. This matter has been investigated in connection with this work, and has been found to play an important part in the determination of the Peltier E.M.F. This question is discussed at some length in the next paragraph. Another probable advantage of this method is that the Joule heating-effect can be made much smaller than has been the case in some of the previous work. In this way the total range of temperature during a single determination is reduced.

Probable Sources of Error.—As will be observed by referring to the data given for the various couples, the compensating currents were frequently quite different. Several causes may be assigned for this, *e. g.*: (1) difference in rate of heat loss to surrounding bodies for the two calorimeters; (2) difference in the resistance of the immersed portions of the metals forming the junctions, due chiefly to the contact itself, and (3) difference in the heat s. This last is due principally to the stirrers either through heat produced by friction in the bearings or unequal stirring. Only the first of these can have any effect upon the final result [see discussion of equation (3)], unless s should vary during the course of the experiment. This may have happened occasionally, but would probably be as apt to influence the final result in one direction as in the other. Once or twice the speed of the stirrers changed owing to bad contact of the brushes with the armature of the motor. This would affect s. But another and more important effect due to such irregular action of the stirrers is that if the speed of the stirrers is varied in any way the steady temperature condition is upset, causing irregular movements of the galvanometer until a new temperature equilibrium is established. This difficulty actually arose and in consequence several runs gave unreliable results.

Inadequate stirring is a very probable source of error. In such cases the heat added to the liquid will not be distributed uniformly throughout the mass, but will remain in the neighborhood of the places where it is produced. In order to test this point a determination of the Peltier E.M.F. for the copper-bismuth couple was made without stirring the liquid. The result so obtained was 0.0084 volt, or a little more than half the true value. This, too, was the cause of considerable annoyance in the case of copper-platinum. Apparently the platinum foil which was used hung too close to the walls of the calorimeters, thus forming a sort of pocket where, owing to the resistance of the platinum, the liquid became hotter than the rest of the liquid in the vessel. Special precautions had to be observed in order to obviate this difficulty before any consistent set of measurements could be made.

To what extent the difference in rate of heat loss of the calorimeters may have affected the results it is difficult to say. One of the original calorimeters was discarded after it had apparently developed a fracture thus becoming a poor insulator. Afterward when some doubt arose as to the equality of this quantity for the two calorimeters which were used in all the later experiments, a test was made as follows: Both the calorimeters with contents were heated to a temperature of 65° C. and left standing uncovered in an atmosphere at 19° C. In 55 minutes the temperature of the calorimeter A had fallen to 30°.4 C., that of B to 29°.6 C. Several hours afterward both had come to the temperature of the surroundings. This shows that their rates of heat loss were practically equal, but these seem excessively large. The very rapid fall in temperature at first was probably due in part to the rapid evaporation of the kerosene at such temperatures. Another reason might be that a considerable proportion of the surface of the liquid was exposed to the air. Granting that even when the calorimeters are at approximately the temperature of the surroundings the quantity h is still rather large, it does not appear from equation (5) that any error in excess of the ordinary experimental errors should arise from disregarding the terms involving h.

SECOND, OR SHUNT-CURRENT, METHOD.

This method differs from the previous method in that compensation is accomplished by sending more current through one of the junctions than through the other, the difference in the Joule heating-effect being equal and opposite to that arising out of the Peltier effect.

Mathematical Discussion.—The mathematical computation of the Peltier E.M.F. in this case is quite similar to that for the preceding case. Using the same notation as before with the proviso that when I_a = current through junction A, and i_a = shunted current, then $I_a - i_a$ = current through junction B, we have

$$\frac{I_a^2R_a - I_aP - h_a\theta_a + s_a}{C_a} = \frac{(I_a - i_a)^2R_b + (I_a - i_a)P - h_b\theta_a + s_b}{C_b}.$$

Clearing of fractions and transposing we have

$$\begin{aligned}(1a)\quad \{(C_a + C_b)I_a - C_ai_a\}P = {}& C_bI_a^2R_a - C_a(I_a - i_a)^2R_b \\ & - \theta_a(C_bh_a - C_ah_b) + (C_bs_a - C_as_b).\end{aligned}$$

Similarly with current reversed

$$\begin{aligned}(2a)\quad \{(C_a + C_b)I_b - C_bi_b\}P = {}& C_aI_b^2R_b - C_b(I_b - i_b)^2R_a \\ & - \theta_b(C_ah_b - C_bh_a) + (C_as_b - C_bs_a).\end{aligned}$$

Adding, we obtain

$$
\begin{aligned}
\{(C_a + C_b)(I_a + I_b) - (C_a i_a + C_b i_b)\}P = {} & C_b R_a\{I_a^2 - (I_b - i_b)^2\} \\
& + C_a R_b\{I_b^2 - (I_a - i_a)^2\} - (\theta_a - \theta_b)(C_b h_a - C_a h_b).
\end{aligned} \tag{3a}
$$

But, if $I_a = I_b$, this reduces to

$$
P = \frac{C_b R_a(2I - i_b)i_b + C_a R_b(2I - i_a)i_a - (\theta_a - \theta_b)(C_b h_a - C_a h_b)}{C_a(2I - i_a) + C_b(2I - i_b)}.
$$

Let us further assume that (1) $2I - i_a = 2I - i_b$, and (2) $C_a + c = C_b$. Then

$$
P = \frac{C_a(R_a i_b + R_b i_a) + cR_b i_a}{2C_a + c} - \frac{(\theta_a - \theta_b)\{C_a(h_a - h_b) + ch_a\}}{(2C_a + c)(2I - i)}
$$

$$
= \frac{1}{2\left(1 + \frac{c}{2C_a}\right)}\left[R_a i_b + R_b i_a + \frac{c}{C_a} R_a i_b - \frac{(\theta_a - \theta_b\left(h_a - h_b + \frac{c}{C_a} h_a\right)}{2I - i}\right].
$$

By applying the binomial theorem and grouping terms as was done for the first method we obtain

$$
\begin{aligned}
P = \frac{1}{2}\Bigg[& R_a i_b + R_b i_a - \frac{(\theta_a - \theta_b)(h_a - h_b)}{2I - i} \\
& + \frac{c}{2C_a + c}\left\{R_a i_b - R_b i_a - \frac{(\theta_a - \theta_b)(h_a + h_b)}{2I - i}\right\}\Bigg].
\end{aligned} \tag{5a}
$$

Notice the resemblance this equation bears to equation (5).

As a sufficiently close approximation for numerical work we may use the simplified equation

$$
P = \frac{R_a i_b + R_b i_a}{2}. \tag{4a}
$$

The assumptions upon which this equation depends are: (1) $I_a = I_b$, (2) $2I - i_a = 2I - i_b$, and (3) disregard of the corrective terms. The first condition is easily realized. The third is the same as that used in deriving equation (4) and nothing further need be said regarding it. In order that the second condition may be assumed without appreciable error it is necessary that I shall be large in comparison with i. Since $P = Ri$, approximately, in order to fulfill this condition the resistance of the junction, R, must be considerable. This is also necessary for a quite different reason. If R were small it would be very difficult to ascertain its value, owing to the effect of the wires leading the current into and out of the bath.

Apparatus.—On this account, for the single determination of copper-nickel each junction consisted of two concentric spirals, one of copper and one of nickel wire. These were wound upon a light fiber frame which just fitted the bottom of the receptacle of the Dewar flask and extended up the sides for a distance of three centimeters. The actual junction was made near the bottom of the vessel. The resistance of each of these junctions was 0.4835 ohm, the wire used being No. 26 copper and No. 23 nickel. The nickel wires in the two junctions were connected by six strands of similar nickel wire twisted together. Heavy copper leads were soldered to the ends of the copper wires. These coils were completely immersed in the liquid. Otherwise the calorimetric arrangements, *i. e.*, stirrers, thermo-elements, etc., were identical with those used for the previous method. For convenience in reading instead of using an ammeter to measure the shunt current it was measured by putting a milli-voltmeter across a standard resistance box through which the current was flowing. The resistance of the voltmeter was 340 ohms. By reading the voltmeter and knowing the box resistance the current could be computed. In most cases a potentiometer would probably be more suitable. By means of a three-way plug-key compensation could be effected in either calorimeter. The electrical connections are shown in Fig. 6, while Fig. 7 represents a cross-section of the bottom of a calorimeter with coil, thermo-elements and stirrer in place.

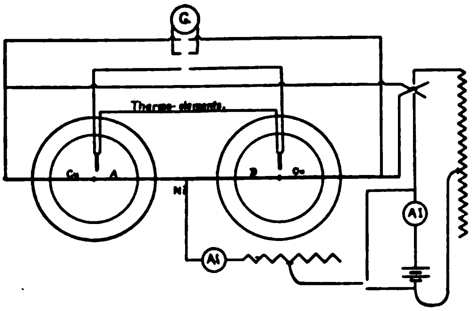

Fig. 6.

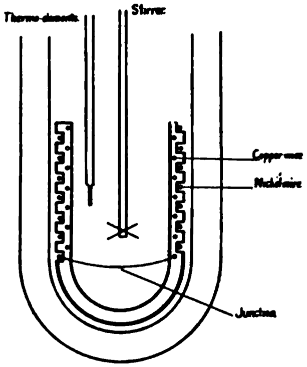

Fig. 7.

Probable Advantages.—An advantage which this method apparently possesses over the other is that the heat required to compensate the Peltier heat is produced in the wires which form the junction where the heat is being absorbed. Owing to the greater heat conductivity of the wires, neutralization of the Peltier effect should be accomplished much more readily than when it must all take place through the liquid. The calorimetric conditions in the two calorimeters are as nearly as possible the same.

Probable Disadvantages.—The total temperature range during an experiment is greater for this method than for the preceding. This is obvious from the fact that the resistance of the junction is very much greater. This might give rise to a greater error since the heat loss is dependent, to a certain extent at least, upon the temperature range. The difficulties attendant upon the stirring are augmented. Otherwise the advantages and disadvantages of this method are substantially those of the preceding method.

EXPERIMENTAL RESULTS.

Copper-Bismuth.

The copper-bismuth junctions were made of two strips of rolled copper plate 2.0×0.24 cm. cross-section, and a strip of bismuth cast for the purpose in the shape of an inverted U. The cross-section of the bismuth was 2.0×0.18 cm. This pair of junctions was the one used for all the preliminary tests of the method. Even the most crude measurements which were made did not differ by more than twenty per cent. from the value which was finally found for this couple. When the "hoop" coils were being used over two hours were sometimes required to determine with a fair degree of accuracy the amount of heat required to compensate the Peltier E.M.F. when the current was only sent in one direction. With the form of the coils finally adopted a complete determination could be made in one and a half or two hours. Four trustworthy determinations were made with the "hoop" coils ($r_a = 3.057$, $r_b = 3.072$),

TABLE II.

Copper-Bismuth.

I	i_a	i_b	$\frac{i_a^2 r_a}{4I}$	$\frac{i_b^2 r_b}{4I}$	P Expressed in Millivolts.
1.037	.1052	.1003	.00816	.00745	+15.61
1.038	.1081	.1015	860	762	16.22
1.957	.1459	.1388	831	756	15.87
.998	.1082	.1014	896	791	16.87
Mean—"hoop" coils					16.14
1.194	.0969	.0845	.00885	.00674	15.59
1.292	.1183	.0661	1219	382	16.01
1.243	.1172	.0664	1247	400	16.47
.502	.0695	.0505	1082	572	16.54
Mean—final coils					16.13

and after these were replaced by coils of the final type ($r_a = 4.503$, $r_b = 4.509$) four other determinations were made. The data and results for these eight determinations are given below and separately averaged. All the values are for an approximate mean temperature of 18° C. Heat was absorbed when the current passed from bismuth to copper, and was given out when the direction of the current was from copper to bismuth. That is, using the same convention as Jahn and others, the sign of the Peltier E.M.F. is positive.

The Peltier E.M.F. between copper and bismuth is, therefore, +0.01613 volt at 18° C.

The extreme variation of these eight determinations is 8 per cent.; hence, the probable error is less than one per cent.

Copper-Silver.

The copper-silver couple was made of rolled copper strips, 1.0×0.25 cm. in cross-section, and a silver strip, 0.9×0.2 cm. in cross-section, rolled from a block of pure silver. Several trial runs were made, but because the magnitude of the Peltier effect was so small no satisfactory results were obtained. The values ranged from zero to + 0.00006 volt. These values are of the same order of magnitude as the experimental errors. The method finally adopted was to determine the rate of change of the deflection of the galvanometer while a compensating current of measurable magnitude was being supplied first to one heating-coil and then to the other. During this time no current was sent through the junctions. Then while no compensating current was being supplied, a current was sent through the junctions in one direction and the deflection at the end of every minute for an interval of from 20 to 30 minutes plotted. From this plot an average rate of change of deflection was obtained. The same was done with the current flowing in the opposite direction. Two such runs were made, the same current being sent through the junctions in each case.

When a current of 0.036 ampere was first sent through the heating-coil in calorimeter *A* and then changed to calorimeter *B* the change in the rate of change of deflection was 0.27 cm. per minute, the resistances of the coils being 4.503 and 4.509 ohms, respectively. From this it follows, as was pointed out in connection with the sensitiveness of the apparatus, that $\frac{0.036^2 \times 4.5 \times 60 \times 2}{0.27} = 2.59$ joules of heat added to one calorimeter will change the deflection of the galvanometer one centimeter.

The results for rate of change of deflection with the current flowing through the junctions were as follows:

TABLE III.

Copper-Silver.

	I	Direction of Current in A.	Rate of Change of Defl. per Min.
First run	4.65	Cu to Bi	+.02 cm.
Second run	4.65	Cu to Bi	+.028
First run	4.65	Bi to Cu	+.01
Second run	4.65	Bi to Cu	+.01

First run — diff. in rate of change of defl. per min. = .01 cm.

Second run — diff. in rate of change of defl. per min. = .018 cm.

Positive deflection indicates that the temperature of A is greater than that of B.

$$P \text{ (First run)} = +\frac{0.010}{0.27}\left(\frac{2 \times 0.036 \times 4.5}{4 \times 4.65}\right) = +\ 0.000023 \text{ volt.}$$

$$P \text{ (Second run)} = +\frac{0.018 \times 0.000023}{0.010} = +\ 0.000041 \text{ volt.}$$

The mean temperature of these two runs was approximately 18° C. The Peltier E.M.F. between copper and silver is, therefore, +0.00003 volt at 18° C. The probable error is less than 0.00001 volt.

Notice that this result is very slightly positive, agreeing with that of Edlund, but is quite different from the value obtained by Jahn (see Table X. below).

A single determination at a temperature of 48° C. gave $P = 0$.

Copper-Aluminium.

The copper strips used were the same ones used in the case of copper-silver. Aluminium wire 0.5 cm. in diameter was used. The ends were flattened so that the immersed portions were 1 cm. wide, thus making their cross-section about the same as that of the silver. Only five runs were made. The first was merely a trial run and is omitted from the following table. The same heating-coils were used as in the previous experiment.

TABLE IV.

Copper-Aluminium.

I	i_a	i_b	$\frac{i_a^2 r_a}{4I} \times 10^8$	$\frac{i_b^2 r_b}{4I} \times 10^8$	P in Millivolts.	Approximate Mean Temp.
4.86	.0436	.0320	.4424	.2375	+.680	13.6° C.
5.12	.0463	.0337	.4713	.2501	.721	16.3
4.00	.0405	.0297	.4614	.2485	.710	18.1
5.60	.0461	.0347	.4271	.2423	.669	15.2
				Means........	.695	15.8

The extreme range of these values is 7.4 per cent. of the mean. The probable error involved is about one per cent. We may, therefore, conclude that for copper-aluminium $P = +0.00070$ at 16° C.

Copper-Platinum.

The same copper strips were used as in the two preceding cases. The most suitable piece of platinum available was a piece of foil about 2 cm. wide and 33 cm. long. Its cross-section was approximately 0.0104 cm.^{2} Considerable difficulty was experienced in getting anything like consistent results with this couple. The difficulty no doubt arose from insufficient stirring of the liquid. Apparently the foil rested against the glass wall of the calorimeter in such a way as to separate a part of the liquid from the main body. This would be heated to a different temperature, and the amount of heat conducted to or from it by the remaining liquid would be dependent upon this difference in temperature. It was only after the greatest precautions had been taken to prevent the reoccurrence of this pocketing effect (such as folding in the corners of the foil and inserting small pieces of cork between it and the glass) that consistent results were obtained. Five determinations were made with the apparatus as finally adjusted. The fifth was a repetition of the second, which gave a result for P of + 0.00121 volt. These two determinations were made with a larger current than was used in the other three cases, and so the difficulty previously mentioned evidently reappeared in the second determination, which has been omitted on that account from the following table of results. In repeating this determination greater care was taken to insure good circulation of the liquid. Heating-coils of 1.49 and 1.505 ohms resistance were used so as to have larger compensating currents.

A current of 0.1097 ampere through the smaller resistance produced a change in the rate of deflection of the galvanometer of 0.494 cm. per minute. From this it follows that 2.18 joules of heat added to one calorimeter would change the deflection of the galvanometer one centimeter.

TABLE V.

Copper-Platinum.

I	i_a	i_b	$\frac{i_a^2 r_a}{4I} \times 10^8$	$\frac{i_b^2 r_b}{4I} \times 10^8$	P in Millivolts.	Approximate Mean Temp.
1.902	.0522	.0326	0.537	0.210	+0.747	17.0° C.
1.533	.0437	.0412	.464	.416	.880	16.3
1.035	.0445	.0195	.713	.138	.851	18.1
2.85	.0546	.0623	.390	.512	.902	17.2
				Means........	.845	17.1

The extreme range of these values is 5.5 per cent. of the mean, hence, the probable error is about one per cent. For copper-platinum $P = + 0.00085$ volt at 17° C.

Copper-Nickel.

The apparatus used in this experiment has been described already in connection with the second method. The first two determinations given below were made on the day previous to the last two, and are considerably higher than the latter. The values corresponding to the higher temperatures are higher than the others, also one compensating current shows a marked tendency to increase with the temperature, the other to decrease. This indicates that the rate of heat loss to the surroundings was not the same for the two calorimeters. On the whole it seems that this method is not as satisfactory as the first method. This is doubtless due to the preponderance of the Joule heat.

TABLE VI.

Copper-Nickel.

I	i_a	i_b	P	Approximate Mean Temp.
0.650	.01463	.00950	+ .00583	19.2° C.
.701	1410	1520	708	25.0
.571	1206	1015	537	19.6
.611	1091	1329	585	24.0
		Means........	603	22.0

The extreme variation of these values is 28.4 per cent. of the mean. Even assuming that the Peltier E.M.F. increases quite rapidly with the temperature the probable error must still be quite large. We shall take + 0.0060 volt to be the value of the Peltier E.M.F. between copper and nickel at 22° C.

SUMMARY OF RESULTS.

The values obtained for the Peltier E.M.F. for the couples investigated are tabulated below.

TABLE VII.

Metal Against Copper.	Peltier E.M.F. Expressed in Millivolts.	Temperature.
—		
Copper........................	——	——
Silver........................	0.03	18° C.
Aluminium....................	0.70	16
Platinum......................	0.85	17
Nickel........................	6.0	22
Bismuth.......................	16.1	18
+		

JUNCTION DEFLECTIONS.

From the junction deflections it appeared that in the case of copper-bismuth the difference in temperature of the junctions at the end of a run varied from 0°.05 C. to 0°.1 C. For copper-silver and copper-aluminium the junctions appeared to have the temperature of the liquid. In the case of copper-platinum the results were variable, but certainly never greater than 0°.1 C. The maximum difference observed for copper-nickel was 0°.16 C.

THERMO E.M.F. AND THE PELTIER E.M.F.

In order to test the validity of Thomson's theorem, which has been mentioned already, viz., $P = T\frac{dE}{dT}$ where E is the thermo E.M.F. at the temperature T, the thermo E.M.F. of the various couples was determined. One junction was kept at a temperature of 0° C. by being

TABLE VIII.

Thermo E.M.F.

Metal Against Copper.	Resist.	Defl. in Cm.	Temp. Diff.	Thermo E.M.F. in Microvolts.	P Computed in Millivolts.
Bismuth........	10,280	27.59	32.70	+55.07	
Bismuth........	7,780	35.84	32.22	54.96	
Bismuth........	7,280	37.43	31.75	54.49	
Mean (Abs. Temp. = 291).......				54.84	+15.96
Silver..........	420	4.76	34.66	+ 0.366	
Silver..........	420	3.92	34.40	.306	
Silver..........	680	.58	32.08	.078	
Silver..........	480	.59	31.02	.058	
Mean (Abs. Temp. = 291)				.202	+ 0.06
Aluminium	680	21.80	29.52	+ 3.07	
Aluminium	420	39.15	31.58	3.11	
Mean (Abs. Temp. = 289).......				3.09	+ 0.89
Platinum.......	3,280	4.72	39.50	+ 2.41	
Platinum.......	1,280	11.19	38.52	2.29	
Platinum.......	2,280	6.00	37.70	2.23	
Platinum.......	3,280	4.01	37.10	2.18	
Platinum.......	1,680	8.20	35.90	2.36	
Mean (Abs. Temp. = 290)				2.29	+ 0.66
Nickel.........	10,280	16.92	49.50	+21.61	
Nickel.........	12,280	13.82	48.54	21.50	
Nickel.........	8,280	19.92	47.22	21.48	
Nickel.........	10,280	15.31	45.14	21.44	
Mean (Abs. Temp. = 295)				21.51	+ 6.35

immersed in a bath of melting ice; the other junction was immersed in a water bath approximately as much above the temperature at which the Peltier E.M.F. was measured as 0° C. was below it. The E.M.F. was measured by connecting the thermo-element in series with a sensitive galvanometer and a standard resistance box. When used with the first three couples its deflection constant was 6.35×10^{-9} amperes per centimeter; with the last two the constant was 6.15×10^{-9}. Its resistance was 280 ohms. The galvanometer was badly damped when only a small resistance was in circuit with it and so the measurements with the copper-silver couple are not very reliable. The second pair of readings given for that couple were taken three hours after the first. The difference is probably due to a change in the temperature of some of the connections. In any event it is certain that the sign of the thermo E.M.F. of this couple was positive. Table VIII. gives the data obtained together with the computed values of the Peltier E.M.F.

COMPARISON OF RESULTS OBTAINED BY DIFFERENT INVESTIGATORS.

In the following table the results of Le Roux, Jahn, Edlund (as computed in the first part of this paper), a few scattered results, and the results of the present investigation are grouped together. The calcu-

TABLE IX.

Results Obtained by Different Investigators, Expressed in Millivolts.

Metal Against Copper.	LeRoux.		Jahn.		Edlund.		Caswell.		Observed by Others.
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
Antimony.	− 5.64	.300							
Iron......	2.93	.224	−3.68	−3.07	− 2.96	− 3.08			−3.06[1]
Cadmium .	.53	.232	.72	.72	.16	.21			
Zinc......	− .45	.614	.68	.41	− .01	− .02			
Copper ...	—	—	—	—	—	—	—	—	—
Silver			− .48	− .58	+ .03	+ .04	+ .03	+ .06	
Gold					.33	.50			
Lead					.50	.57			
Tin					.56	.82			
Aluminium					.70	.89	.70	.89	
Platinum .			+ .37	+ .38	1.02	1.23	.85	.66	
Palladium.					2.17	2.43			
Nickel....			+5.07	+5.44			6.0	6.35	+6.75[2] +8.04[3]
Bismuth ..	+22.3	.263			+17.7	+17.6	+16.1	+16.0	

[1] Lecher's derived value of the Peltier E.M.F. between iron and *silver*.

[2] Barker.

[3] Cermak.

lated values have been obtained by means of Thomson's equation. The second column of values given for Le Roux contains the ratios of his values of the Peltier E.M.F. to thermo E.M.F. in relative units.

For all of these values I have aimed to retain only as many significant figures as seem to be justified by the accuracy of the experiments.

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April, 1911.

THE RECOVERY OF THE GILTAY SELENIUM CELL AND THE NATURE OF LIGHT-ACTION IN SELENIUM.

BY F. C. BROWN.

IN the July number of the PHYSICAL REVIEW[1] it was shown that the general behavior of the four known varieties of selenium under the action of light could be explained by assuming that the different varieties were merely differently proportioned mixtures of three components which were in equilibrium according to the reaction

$$A \rightleftarrows B \rightleftarrows C.$$

In these considerations only the B component was a conductor of electricity. The amount of change of conductivity under the action of light at any instant was supposed to be proportional to the amounts of the changing components and to the rates of interchange according to the equations,

$$dB/dt = -(\alpha_2 + \beta_1)B + \alpha_1 A + \beta_2 C, \tag{1}$$

and

$$di/dt = kdB/dt, \tag{2}$$

and the value of the conductivity at any time after illumination was calculated to be

$$i = L/N + c_1 e^{m_1 t} + c_2 e^{m_2 t}, \tag{3}$$

where L, N, c_1, c_2, m_1, and m_2 represent constants for a light of a given intensity when the temperature and other functioning conditions are unchanging. These constants are determined solely by the rates of interchange as shown. The method of procedure was to assign values for the rates of interchange and then compute the value of the conductivity for different times of exposure. By the use of rates properly chosen such constants were obtained for equation (3) that its graph could be made to conform in a general way with all of the curve forms obtained experimentally with the four known varieties of selenium. It was stated that the action of light was merely the alteration of the rates of interchange, particularly an increase in the values of the direct rates of change α_1 and β_1, and further that the recovery from light-action was merely the process of restoration of the equilibrium amounts of the A, B and C kinds of selenium as the result of the smaller values of α_1 and β_1 prevailing in the dark.

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[1] PHYS. REV., XXXIII., p. 1.

Therefore in the recovery of selenium equations (1), (2) and (3) must likewise be in agreement with the changes taking place, provided the proper values are assigned to the rates of interchange, and new limits are used in the integration such that

$$c_1 = \left[\frac{C_1}{\beta_1} + \left(\frac{L}{N} - B_1\right)\frac{1}{\beta_2 + m_2} - \frac{L}{N\beta_2}\right]\left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_2 - m_1}\right]$$

and

$$c_2 = \left[\frac{C_1}{\beta_1} + \left(\frac{L}{N} - B_1\right)\frac{1}{\beta_2 + m_1} - \frac{L}{N\beta_2}\right]\left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_1 - m_2}\right],$$

where B_1 and C_1 are the respective amounts of the B and C kinds at the instant the recovery begins. In the action of light the corresponding constants B_0 and C_0 represented the amounts of the same components when the selenium was in equilibrium in the dark.

Inasmuch as only the B component is conducting we may simplify our discussion by supposing that the units of conductivity are of such magnitude that B may be used interchangeably for either the amount of the component or the conductivity.

Whereas it was shown in the previous paper that the general behavior of all the known varieties of light-positive and light-negative selenium could be explained by the proposed theory, it will be shown in this paper for one of the light-positive varieties, viz., that found in the Giltay selenium cell, that the change of conductivity during both exposure and recovery can be explained quite accurately by the same theory. The Giltay cell furnishes evidence more convincing than some varieties of selenium in that some of its rates of interchange are very close to the critical values. A slight alteration of the rates by certain temperature changes will transform the experimental recovery curve from one type to a second distinct type of curve. And it will be shown that these two types of recovery curves are precisely what might be predicted from theory. The Giltay cell is particularly adapted for a critical test of the theory also because of its stability, sensibility and uniformity. If kept in the dark most of the time and subjected to no unusual treatment the selenium cells of the high resistance type made by Giltay maintain approximately their initial resistance and initial light-sensitiveness. It is thought that any work with the Giltay cell can be repeated with greater certainty than can work with any other light sensitive selenium on the market. As many can testify a special skill is required to produce selenium with specific rates of change. Mr. Giltay states that after making selenium cells for thirty years he still has surprises in his results. My high sensibility selenium cells are more sensitive than the Giltay cells but they possess neither stability nor uniformity. The selenium cell used in these analytical investigations is the same one mentioned in the preceding paper.

Exposure and Recovery Curves.

Selenium is difficult to investigate in that so many agencies alter its conductivity, and it is not always easy to eliminate all except the one under investigation. For example in studying light-action, there is a certain heating effect and also a change in the pressure on the selenium. The change in pressure may be due to change in volume of the selenium between the semi-fixed electrodes, as a result of the light-action and the temperature-action. The magnitude of these two effects is not easy to ascertain. In our theory we must consider these effects as due directly to light-action. Probably the effects just mentioned are not larger than the observational errors. In addition the radioactivity of the atmosphere, the moisture, and the barometric pressure alter the equilibrium condition and consequently the conductivity. In order to minimize the disturbing influences the selenium cell was placed in a kerosene oil, or paraffin oil, bath which was kept in motion continuously during observations by a stirring device. See Fig. 1. The kerosene oil bath was surrounded by a water bath which was also kept in motion by a stirring device, run by a motor. The temperature of the bath was regulated by an electric heating coil. The source of illumination was a 24 watt tantalum lamp with frosted globe. The lamp was inverted in a beaker which stood in the water bath. Unless otherwise mentioned the distance of the lamp was kept fixed at about 10 cm.

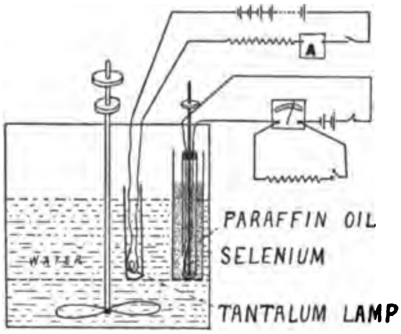

Fig. 1.

The intensity of the light was regulated by varying the resistance in series with the lamp. The large bath was kept light tight. It was considered that the advantages of this apparatus were that the selenium would remain at about constant temperature during observations and that all the surroundings except the lighted lamp would be at the same temperature as the selenium. There were fewer difficulties due to stray light than I have observed hitherto with other apparatus. The conductivity was read directly from a Siemens and Halske needle galvanometer in series with the selenium cell and a two volt storage battery.

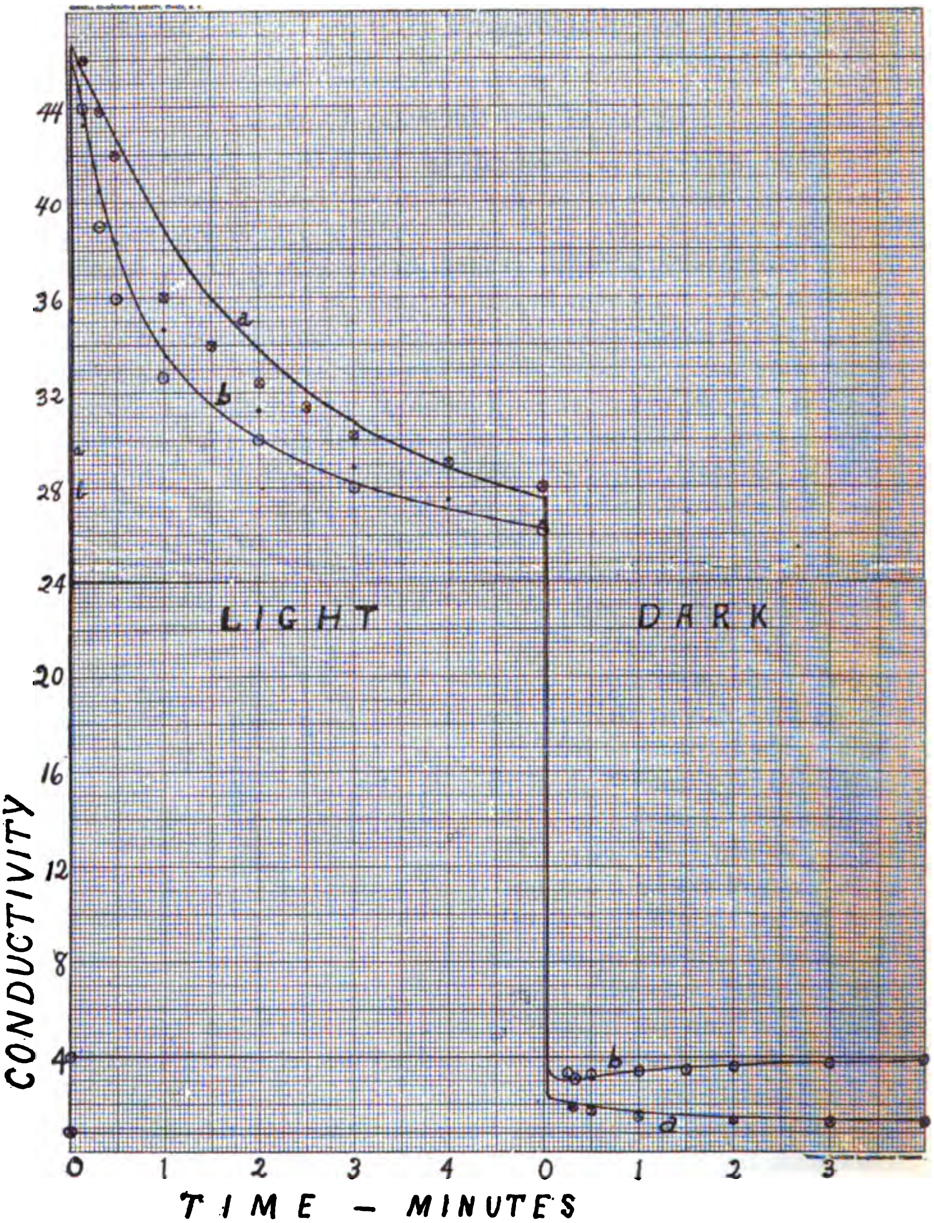

Fig. 2.

a represents the theoretical values of the conductivity during exposure and recovery at 18° C.; *b* is the theoretical curve for 52° C.; ⊗ represents the observed values of the conductivity at 18° C.; ⊙ represents the observed values at 52° C.; ● represents observed values at 28° C.

Observations were taken with the selenium at 18° C., 28° C., and 52° C., when the intensity of the illumination was that given by the tantalum lamp when the heating current was 0.43 ampere. The observations are shown in Fig. 2. It was impossible with the apparatus described to observe the more rapid changes which took place within a fraction of a second. The rapid changes due to the same illumination were measured by another method to be mentioned later in the paper. It may be noted that the conductivity under intense illumination is almost independent of the temperature. At the higher temperature the decrease of conductivity occurs somewhat more rapidly thus bringing the conductivity below that at lower temperatures. This may seem rather strange when it is noted that the conductivity at 52° C. begins at 4.0, which is five times that at 18° C., and two times that at 28° C. These facts are in substantial agreement with the results published in the previous paper, under less favorable circumstances. The maximum change of conductivity at the lowest temperature is about 110 times that in the dark, while the equilibrium conductivity is only 63 times that in the dark.

The recovery for the three temperatures is remarkably different. At 18° C. the first observation that could be made accurately was after 20 seconds, when the conductivity was more than twice that required for equilibrium in the dark. Although readings could not be taken accurately before 20 seconds, yet it was certain that at the end of the fifth second that the conductivity was not more than three times the dark value. After the first few seconds the remainder of the conductivity was regained very slowly. After four minutes it was fifty per cent. too high and after ten minutes the conductivity was yet 40 per cent. above the final value. In the recovery at 28° C. there was no observed difference in the rapid change but the slow change became much faster. After 15 seconds the conductivity was only 47 per cent. above the final value and after four minutes it was only eight per cent. The results that show that the rapid change taking place during recovery is not altered much by temperature will be given later.

At 52° C. the first observation that could be made showed that the conductivity was less that the final value as shown by curve *b*, Fig. 2. In fact it was about 25 per cent. too low for equilibrium. By further observations as shown in the same figure, the conductivity increased slowly during recovery until the equilibrium value was reached. After four minutes the value was 7 per cent. below equilibrium and after 8 minutes it was 5 per cent. Roughly the conductivity seems to increase during recovery only slightly faster than it decreased at the lower tempertures. But how much the difference is depends upon the temperature.

At some temperature between 28° C. and 52° C. the selenium is in what might be called a critical condition, so far as the slow changes are concerned in the recovery. The slightest alteration in pressure, temperature, or other influencing agents might change the character of the recovery curve. In fact the selenium may be said to be in a critical condition at either 28° C. or 52° C. for a ten second exposure at 52° C. will give a recovery curve of like character to the one shown in Fig. 2 for 28° C.

These two types of recovery in the Giltay cell which are conditioned by temperature are very striking and they offer a rather severe test to our theory. However these diverse types can be explained theoretically by assuming that the action of the temperature change is merely an alteration of the rates of interchange. This was predicted in the previous paper referred to. In Table I. are given the rates of change during exposure and also during recovery which will explain the curves as obtained from observations when the selenium was at 18° C. and also at 52° C. The constants and the equations of conductivity result from

Table I.

Giving the rates of change necessary to explain the observed values of the conductivity during exposure and recovery at different temperatures.

	18° C.	
	During Illumination.	During Recovery.
α_1	.054	0.00134
α_2	12.0	12.0
β_1	0.9	.018
β_2	0.004	.004
A	5,550 Equilibrium values in the light.	11,200 Values for complete recovery.
B	25	.8
C	5,625	3.6
Equation of conductivity	$B = 25 - 46.2e^{-12.5t} + 22e^{-.0075t}$	$B = 0.8 + 24e^{-12t} + 1.25e^{-.004t}$
	52° C.	
	During Illumination.	During Recovery.
α_1	0.3	0.025
α_2	12.0	12.0
β_1	0.3	.07
β_2	0.009	.009
A	1,040 Equilibrium values in light.	1,892 Equilibrium values in the dark.
B	26	4
C	860	30
Equation of conductivity	$B = 26 - 42e^{-12.6t} + 20e^{-.016t}$	$B = 4 + 23.1e^{-12t} - 1.1e^{-.01t}$

the rates of change, when calculated by the aid of the set of equations given in the previous paper and in this paper. Other rates might satisfy the experimental curves as well as the ones chosen. I can only state that the ones recorded are the best I could find. Everything depends on the rates. The quantity of only one kind of selenium must be taken arbitrarily to suit the units of conductivity chosen. The quantities of the other kinds both in the dark and in the light are calculated. As stipulated the sum of the three kinds can not change. In practice the value of the B kind for equilibrium in the dark was chosen to agree with the observed conductivity of the selenium in the dark. Then rates of change were found which would give the maximum and the final conductivity observed in the light. After obtaining agreement between theory and experiment for exposure it was fortunately very easy to obtain the same agreement for recovery. Afterthought showed that this is what should be expected. In fact if perfect agreement were obtained for exposure, then we should know almost without trial what rates should be proper to explain the recovery observations. The recovery and exposure, as a study of the theory will show, are closely correlated. The graphs of the equations in Table I. are represented in Fig. 2 by the continuous curves. It will be observed that the conductivity curve is always continuous.

It is surprising indeed that the agreement between theory and experiment is so close as shown in Fig. 2. This particular case was chosen as the most difficult one to explain that could be obtained with any variety of selenium under any conditions. The extreme range of the conductivity and the peculiarity of the curves would have made a much worse agreement satisfactory. It is not certain that the rates given in Table I. are more than approximately correct. However later thought shows that they are of the right order of magnitude and probably vary only in the second place from the true values. But what is most important at this stage of our investigation is to find out what light and temperature do to the rates of change, and to inquire if the things that happen are consistent and reasonable. It may merely be noted here from Table I. that light increases the direct changes α_1 and β_1 and that a temperature rise increases all the changes except possibly the reverse rate of change α_2. The relative action of light and temperature as shown is of much interest but we shall reserve discussion on this point until later in the paper when we have considered more comprehensive data.

CHANGE OF CONDUCTIVITY DURING EXPOSURE AND RECOVERY FOR FAINT ILLUMINATION.

In the discussion just preceding the intensity of the light may be considered as relatively great although it was probably not larger than 32 cp. at 10 cm. In general it is important to check theory and experiment under conditions that allow the greatest change, but in this instance it is also quite necessary to find agreement where the illumination is not intense and where there is consequently only a small change in the conductivity.

In order to predict what difference may be expected between faint illumination and intense illumination, we must first define what we mean by faint and intense. We will consider the wave front of light as speckled at any instant with light and dark spots of small dimensions, and that the light spots travel about over any uniformly illuminated surface in such a manner that after a few seconds any one finite area shall have been hit by the same number of light spots as any other equal area on the surface. This is the well known spotted wave front theory[1] proposed by Sir J. J. Thomson,[2] and others. The intensity will be defined as the average number of light spots per unit area at any instant. Thus the essential difference between the action of an intense light and a faint light on selenium lies in the difference in the number of particles acted on at any instant, or we may say in the difference of rate of action. If light acts on selenium until saturation is produced there will be just as many particles struck and changed by light per second as recover per second. Light of small intensity acts on only a small number of particles per second, while an intense light acts on a relatively large number. Every particle that is struck with faint light will change just as much as it would if struck by an intense light, but before it is struck a second time it will be almost recovered. The interval between successive impingements of a faint light on the same small region is relatively large. And so on the average for all the particles, they will be almost recovered all the time. The result is that the rates of recovery for faint illumination will be smaller than for intense illumination. More will be said on this point in the discussion of the experimental results obtained.

The observations with faint illumination were taken under about the same circumstances as those previously described with intense illumination. The source of light was the same tantalum lamp when it was carrying 0.11 ampere as heating current. As before the entire surface of the selenium was illuminated. The intensity was so regulated that the conductivity would be about doubled by the light. The temperature was about 26° C. The observed conductivity at all times during both exposure and recovery is shown in Fig. 3. In Table II. are given the rates of change during exposure and recovery which would cause the conductivity to vary along the continuous lines *a*, *b*, and *c*. The agreement is found to be within the limits of experimental error and is as good as could be hoped for. It is particularly noteworthy that the same rates of change explain the recovery at the end of a ten-second exposure that explain the recovery at the end of a ten-minute exposure.

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[1] See paper by Sir J. J. Thomson.

[2] Proc. Camb. Phil. Soc., XIV, p. 41, 1908.

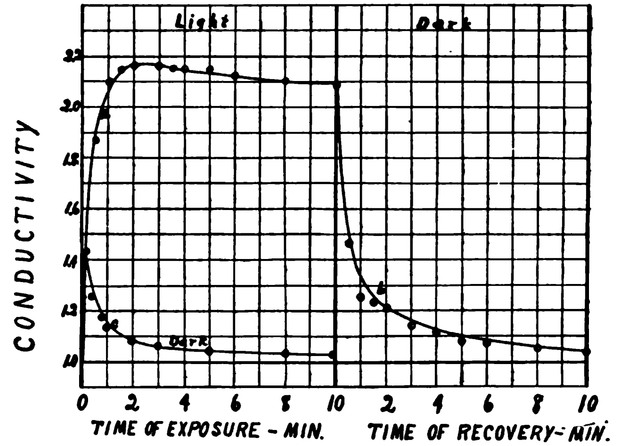

Fig. 3.

Exposure and recovery curves with faint illumination. *a* is the theoretical curve for exposure; *b* and *c* are theoretical curves for recovery; ⊙ represents the observed values.

Table II.

Giving the constants and resulting equations necessary to explain the exposure and recovery curves when the selenium is exposed to faint illumination at 26° C.

	During Illumination.				During Recovery.	
α_1	0.004				0.00132	
α_2	0.02				0.02	
β_1	0.01				0.0053	
β_2	0.003				0.003	
A	15.6	Before illumination.	10.2	Values at end of ten min. exposure.	13.9	Values at end of ten sec. exposure.
B	1.0		2.86		1.42	
C	1.8		5.4		3.11	

$B = 2.06 - 1.17e^{-.033t} + 0.17e^{-.003t}$. $B = 1 + 0.83e^{-.03t} + 0.23e^{-.0030t}$ for 10 min. exposure.

$B = 1 + 0.35e^{-.03t} + 0.08e^{-.0026t}$ for 10 seconds exposure.

The initial values of the three kinds of selenium for recovery after a ten-second exposure are calculated by the aid of the equations given in the previous paper. It must be remembered that the initial conditions during recovery are determined by the rates during illumination and conversely that the initial conditions during exposure are dependent on the rates during recovery, as well as the time of recovery. No experiments were made to check theory and experiment where the selenium had only partially recovered but I have no doubt whatever but that the agreement would be as satisfactory as the other results.

The Recovery with Different Durations of Exposure.

We have shown for intense light at certain temperatures and for a given period of illumination that the reverse change between the A and B components is large compared with the reverse change between B and C. This suggests at once that the recovery of B into A may be determined directly by measuring the resistance changes over such short intervals of time that no appreciable amount of the C kind is changed into B. In order to predict what change in B may be expected, we will substitute the rate values during recovery and also the amounts of the components, as found in Table I. into equation (1). This gives

$$dB/dt = -(12 + .14) \times 25 + 0.0025 \times 1923 + 0.004 \times 100.$$

We observe from this that so long as B is large compared with unity, that the change in B should be almost proportional to the amount of B present at any instant, regardless of the amount of A and C. This conclusion may obviously be stated in the following form: the change of conductivity for short intervals during recovery divided by the conductivity should be a constant for large values of B and constant illumination.

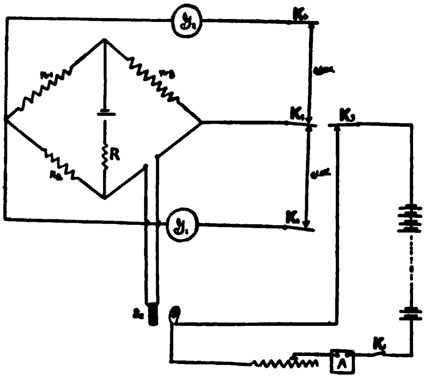

Fig. 4.

To test the above relation the selenium was exposed to the tantalum lamp, carrying 0.35 ampere, for various lengths of time, and the mean conductivities were measured during the last 0.1 second of exposure and during the first 0.1 second of recovery. This was accomplished by a modification of the method of measuring fluctuating resistances described by Brown and Clark.[1] Two galvanometers instead of one were used, as shown in Fig. 4. The pendulum that operated the galvanometer keys also opened the lighting circuit. The first galvanometer was thrown into circuit only during the last 0.1 second of exposure and the second galvanometer was likewise in circuit only during the first 0.1 second of recovery, after the selenium was darkened. By the usual calibration the deflections were translated into the equivalent mean conductivity during the interval in question. The period of one of the galvanometers was increased by adding a lead rider to the moving coil. This enabled one observer to read both galvanometers. The selenium cell was left in the bath arrangement previously described. The temperature was 22° C. An hour or more elapsed between observations to allow the selenium to recover. The results of the observations are shown on the curves in Fig. 5. The points on the upper curve resulted from observations made on the first galvanometer, and the points on the lower curve were calculated from the deflections of the second galvanometer. The difference between any pair of observations recorded on the two curves divided by the higher value gives the mean fractional part of the conductivity recovered between zero and 0.1 second. This fractional part or per centage recovery is recorded in Fig. 5 for each pair of observations. I was surprised myself at the constancy of these percentages. The conductivity varies by at least forty per cent. and yet it is doubtful if the percentage recovered varies as much as one per cent. when the time of exposure varies from 0.4 second to 240 seconds. As the first value is low however there may be some doubt as to the constant percentage recovery for exposures of only a fraction of a second.

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[1] Phys. Rev., XXXIII., p. 53, 1911.

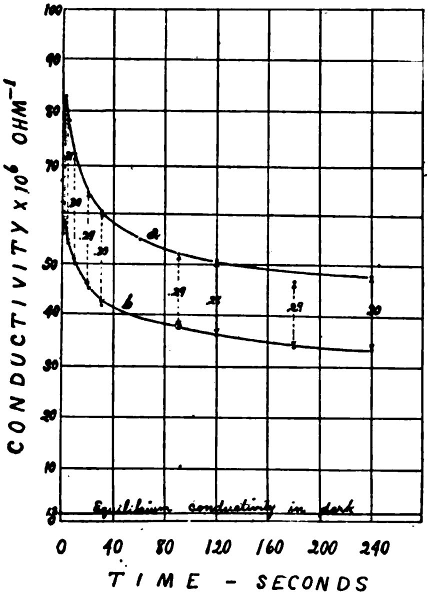

Fig. 5.

The upper curve (*a*) shows the conductivity for any period of illumination from 0.4 second to 240 seconds. The lower curve (*b*) shows the conductivity of the selenium after recovering 0.05 second following any period of illumination. Conductivity in dark 1.3.

The mean percentage recovery recorded during the first 0.1 second was about 30. If we assume that this value was reached in 0.05 second, then we obtain for the rate of change of B into A, $\alpha_2 = 12$. This is in agreement with the curves in Fig. 2, for which no observations were taken directly for periods less than ten seconds. In fact the result here recorded was used as an aid to obtain the correct rates of change to explain the observations in Fig. 2. By the same method recorded in this section the recovery during 0.1 second was measured at 40° C., and it was found that the fractional part recovered was 34 per cent. This indicates quite directly what was shown in Table I., that the value of the reverse rate of change α_2 is altered little if any by temperature changes.

In Fig. 6 is shown the percentage recovery for exposures between zero and six seconds. In taking these recorded observations the selenium was not placed in a bath, but nevertheless they are substantially in agreement with the other results. The intensity of the light was less than in the other instance, and the pendulum keys were so arranged as to give the recovery after 0.1 second and not the mean recovery between 0 and 0.1 second.

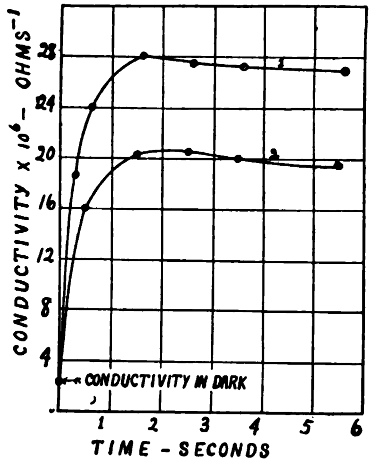

Fig. 6.

(1) Conductivity before recovery. (2) Conductivity after recovering during 0.1 sec.

The Variation of the Rate of Recovery with the Intensity of Exposure.

A comparison of the data in Tables I. and II. indicates that the rapid rate of change α_2 varies greatly with the intensity of illumination. After the thorough investigation mentioned in the last sections was made, which showed that the value of α_2 did not vary with the time of exposure within very wide limits, it was thought advisable to investigate the effect of varying intensity by the same method. The same apparatus referred to in Fig. 4 was used. However, when the change of resistance was small the first galvanometer was used to measure the equilibrium resistance in the dark and the resistance at the end of a three minute exposure by the ordinary Wheatstone's bridge method. The second galvanometer measured by its throw the mean change of resistance during the first 0.1 second after the light was extinguished. The period of illumination was kept constant and the intensity was varied by changing the heating current in the lamp. As I have not yet considered quantitatively the effect of varying the intensity of the light, I have not yet taken the trouble to interpret the intensity in the usual units. A sufficiently accurate notion of the intensity for our present discussion may be estimated from the value of the heating current and also from the change of resistance of the selenium. The results of the investigation are given in Table III.

Table III.

Time.	Current in Lamp Amperes.	Temperature.	Potential Across Cell, Volts.	Time of Exposure.	Resistance in Dark.	$1/B$ Resistance in Light.	Deflection.	$\Delta B \times 10^8$ Ohms^{-1}.	$\frac{\Delta B}{B}$ Mean Percentage.
10:55 A. M.	0.15	27.8°C.	2	3 min.	680,000	159,000	6.1		
11:45					680,000	158,000	4.0		
1:00 P. M.					700,000	156,000	4.0		
						Mean	3.7	0.016	2.5
9:02 A. M.	0.20	28.0	2	3	740,000	74,000	14.5	0.11	
9:53					710,000	74,000	14.6	0.11	
									8.2
1:15 P. M.	0.45	27.5	2	3	700,000	16,300	74.		
3:50					677,000	16,900	73.		
								2.79	46.5
6:30	0.33	27.7	2	3	703,000	28,200	64.	1.05	29.6
7:25	0.355		2	3	710,000	23,000	73.	1.44	33.1
9:40	0.40	27.9	2	3	680,000	19,700	76.8	2.04	40.2
10:55	0.3	27.5	2	3	705,000	34,000	67.0	0.72	24.0
12:04	0.25	27.8	2	3	683,000	49,400	39.3	0.31	15.3
2:38	0.22	28.1	2	3	660,000	62,000	28.0		
5:30							24.0		
								0.18	11.2

The value of $\Delta B/B$ varies from 2.5 per cent. for the faintest light measured to 46.5 per cent. for the most intense light. It may be stated without qualification that $\Delta B/B$ increases with increased intensity. The rate of change as calculated from the value 0.025 is only slightly larger than the value given for α_2 in Table II., where the conductivity was somewhat less. This is as it should be.

In obtaining the data in Table III. the character of the light varied as well as the intensity did, and the same may be said for the comparative observations in Figs. 2 and 3. Just what difference arises from the altered character of the light can not be predicted with any certainty, but the assumption that the characteristic difference in the results noted is due to a variation in the light intensity can not be far wrong. It was shown in the previous paper[1] in a general way that when the character of the light source was practically constant, and when the intensity of illumination was varied by varying the distance of the source that the time required for the maximum conductivity to be reached during exposure increased with decreasing intensity.

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[1] Phys. Rev., XXXIII., p. 1.

The Effect of Short Exposures.

The effect of short exposures to either intense or faint illumination is to produce the changes that take place rapidly but it does not follow that the recovery should be correspondingly less for short exposures, than it would be for long exposures. If there is a large increase in the conductivity as a result of a short exposure, during exposure the conductivity component changes both into the *A* kind and the *C* kind, and it will be noted from Table I. that the rate of transformation into *C* is relatively quite large. It follows that before equilibrium is reached all of the *C* kind must be retransformed back into the *B* and *C* kinds, which is of course a slow process. Again this notion is confirmed by the equations of the conductivity, in which the exponential coefficients are determined solely by the rates of change, while the constants c_1 and c_2 are determined both by the rates of change and the time factor.

That the preceding explanation for the recovery from short exposures is probably the correct one, may be inferred further from the observations shown in the curves in Fig. 7. The selenium at 20° C. was exposed to a very intense light, roughly a 32 cp. tungsten lamp at 7 cm. distance for a period of 0.35 second. This period was just about sufficient to allow the selenium to reach its maximum conductivity, *i. e.*, the condition when there was the maximum amount of *B* present. This was one hundred times the amount of *B* present in the dark equilibrium condition. After 0.85 second only about 85 per cent. of the conductivity change is seen to be recovered. And even after 60 seconds it was still twice what it should be for equilibrium in the dark at that temperature. Probably the most surprising fact is that both theory and observation show that it requires longer for selenium to recover its conductivity after exposure to a faint light than it requires to recover from a long exposure to a very intense light.

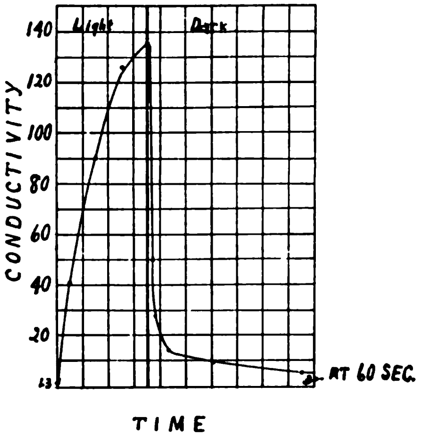

Fig. 7.

Each division represents 0.1 second.

For high temperatures also the recovery from very short exposures is similar to that shown in the last figure, but more rapid. But for longer exposures the recovery is like that shown in Fig. 2. This is in general agreement with the theory. For short exposures there is only a small amount of the *B* kind transformed into the *C* kind and consequently the conductivity should be continually diminishing. If the exposure is continued then there is such a large amount of the *C* kind produced that the *B* kind first diminishes rapidly below the dark value in order to approach equilibrium between *A* and *B*, and then increases slowly until the equilibrium value is reached. Here caution is urged against assuming that selenium is in equilibrium merely because the equilibrium value of the conductivity is reached. In case the selenium is in apparent equilibrium, but in reality not, the sensitiveness to light is diminished just as might be expected if the amount of the *A* kind present were too small. For a long time this diminished sensitiveness to light was very puzzling to me.

THE RECOVERY FROM THE EFFECTS OF HIGH POTENTIAL DIFFERENCES.

It was stated in two earlier papers[1] that the change of conductivity of selenium by high potential differences was of the same nature as the change by light This conclusion was based largely upon the fact that the light sensitiveness of the selenium diminished as the potential difference between the electrodes was increased, and also upon the fact that both agencies acted in such a manner as to first increase the conductivity and then to decrease it. Further consideration shows that both effects

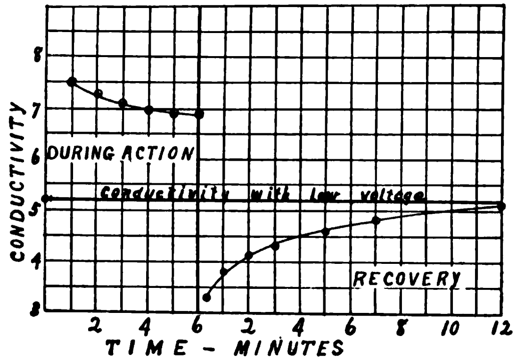

Fig. 8.

Curves showing the conductivity of the selenium during the action of 152 volts potential difference and during the recovery.

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[1] PHYS. REV., XXVI., p. 273, 1908, and XXXIII., p. 1, 1911.

are similar, in that they alter the rates of interchange and consequently increase the amounts of the *B* and *C* kinds. But the rates are altered in quite different proportions by the two effects. Light acts chiefly on the rates between the *A* and *B* components while the high potential acts about as much on the *B* and *C* components as on the others. Observations that were taken during action and recovery with 150 volts are shown in Fig. 8. I have not yet succeeded in obtaining any accurate notion of the rapidity of the more rapid change. Before an accurate comparison of the rates can be made it will be necessary to measure the rapid changes.

THE INTERPRETATION OF THE RESULTS.

We have shown that the proposed kinetic reaction theory agrees in a general way with all the varieties of selenium known and further that when tested in particular with one of the most complicated the agreement is all that could be hoped for. It has not been necessary to impose any conditions that are unreasonable or that complicate the simplicity of the argument. But having established the theory thus far to a fair degree of accuracy, it is of interest to inquire what may be its further physical significance.

It has not been necessary to assume that more than one of the three components are conducting and further it has not been necessary to assume that light acts in the least degree on the reverse rates of change. In both these respects the theory is less complex than when it was first proposed. These facts have been tested for intense light at two widely varying temperatures. In fact the temperature difference was so great that the initial conductivity in the dark differed by a factor of five. The light was so intense that the conductivity in one instance had a maximum value 110 times that in the dark. That only the direct changes are necessarily altered by light was also shown for light so faint that the maximum conductivity was only twice what it was in the dark. There can be little doubt but that for light effects one hundred times smaller than this, we would also find that only the direct rates would necessarily be altered. The generality of this conclusion is not only interesting but also a big advance in our theory. It should simplify the physical interpretation and at the same time reduce the difficulties in the mathematics.

TABLE IV.

Ratio of Rates in Light to Dark.	Intense Light at 18° C.	Intense Light at 52° C.	Faint Light at 22° C.
α_1'/α_1	40	12	3
β_1'/β_1	50	4.3	1.9
α_2'/α_2	1	1	1
β_2'/β_2	1	1	1

That light may act on the rates in about the same way for intense light as for faint light is shown in Table IV., which is compiled from the data in Tables I. and II. To distinguish between rates, those prevailing during light action are primed.

Attention should be called to the fact that at different temperatures and with different intensities of light, we do not suppose the existence of the same total amount for the three components. The meaning of this is not certain. The total amount might possibly vary with temperature but this could hardly be the case with varying intensity. Possibly the amounts considered are partially fictitious, and that as previously alluded to, an intense light acts on a large proportion of the components present, while a faint light acts on only a relatively small proportion at any instant. It may be suggested here that the different initial rates of change that analysis shows to exist in the four known varieties of selenium, may in some cases arise from a difference in the attractive power of the components for certain molecular aggregates either in the solid or gaseous state. Obviously the impurities might modify the rates unequally for the different components. I hope to develop this idea further later in explaining certain unstable samples of selenium.

In the original paper it was assumed that the light was of uniform intensity throughout the selenium at any instant. Now in order that our analysis shall apply to the facts, we must understand that the light shall have what might be called only an average uniformity.

The rates of change that are given in this paper assume that light acts throughout the conducting layer of selenium. The fact that the rates are so consistent with each other and that they so satisfactorily explain the observations would lead one to suspect that the above assumption is not far wrong.

The Effect of other Agencies.

A study of the tables shows that our previous predictions concerning the similarity of the action of light and temperature still seem to be consistent. So far as light action is concerned it is necessary to assume that temperature alters the direct rates α_1 and β_1 to a very large degree. However in addition to this, temperature produces a slight change in the reverse rate β_2 and possibly also a minor change in conductivity of which no account is taken in our theory. The fact that temperature alters three of the rates will probably make it easy to explain the numerous temperature coefficients that are possessed by the different varieties of selenium. Temperature no doubt acts throughout the conducting layer of selenium. This being assumed we have at once an easy method of estimating the relative depth of penetration of selenium by light.

The behavior of selenium under the action of pressure, radium, X-rays and other agencies should aid us in the interpretation of our results. The fact that selenium recovers very slowly from radium action as pointed out by Brown and Stebbins or X-ray action as pointed out by Miss MacDowell[1] can be explained satisfactorily if we assume that these agencies have compared to intense light a low frequency for any point region. It seems that this is the most reasonable assumption to make. Further if selenium is suddenly relieved from a very high pressure it should recover much more rapidly for the rapid part of the change, than it does from illumination of ordinary intensity. What observations we have made on this point indicates this high rapidity of recovery for either small or large pressures. However, we were not prepared in 1907 to measure this rapid rate. Further investigations on the rate of action by other agencies will no doubt show that the proper assignment of rates of interchange will explain the larger part of the changes taking place, but the values that are obtained may modify our intrepretation materially.

Summary of Conclusions.

1. Without making any allowance for the fact that the light does not probably penetrate throughout the conducting layer of selenium, the theory agrees fairly satisfactorily with the observations over a wide range of temperature and light conditions.
2. Only one of the three components is conducting.
3. Very direct experiments show that for at least one case the change in the conductivity is proportional to the amount of the changing component.
4. Temperature action in the Giltay selenium cell is essentially the same as light action but not identical to it.
5. More careful and more extensive work should be carried out to determine the full significance of all the rates of interchange.

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[1] Phys. Rev., XXX., p. 474; also paper by M. Perreaux, Comptes Rendus, Vol. 129, p. 956.

THERMAL CONDUCTIVITY AT HIGH TEMPERATURES.

By M. F. Angell.

Introduction.

With the growth of the electron theory and its application to the flow of heat in metals the measurement of thermal conductivity becomes of greater interest. The determinations, up to the present time, have been confined within narrow limits of temperature and the object of this investigation was to determine the thermal conductivity of a few metals over a wide range. The first measurements at high temperatures were made by Forbes,[1] using the well-known "Forbes bar method," on wrought iron at temperatures of 0°, 100°, 200° and 275° C.; giving a decrease in thermal conductivity from .207 at 0° C. to .124 at 275° C. Tait[2] and Mitchell[3] used the same method, but found an increase in conductivity with temperature, which is undoubtedly in error, as shown by the later work of Jäger and Diesselhorst.[4] Lorenz[5] heated a rod at one end by contact with a large slab and determined the temperature gradient by means of thermocouples inserted in holes along the rod; the source of heat was then removed and the temperature gradient determined when the rod was cooling. Between 0° C. and 100° C. he found an increase in conductivity with temperature for aluminum, brass, copper and german silver; a decrease for antimony, bismuth, cadmium, iron, lead and zinc; and a constant for magnesium. Baillie,[6] with the Forbes method, determined the thermal conductivity of nickel between 0° C. and 100° C. to be .132 and found this value to be changed only in the third decimal place at a temperature of 200° C. Jäger and Diesselhorst[4] used a method suggested by Kohlrausch,[7] which consisted in heating a rod with a constant electric current; the ends of the rods being in contact with large baths, a steady flow of heat was maintained from the center to the ends. The temperature was measured at three points along the rod by means of thermocouples inserted in holes. Determinations were made on a large number of materials at 18° C. and 100° C.; an increase in thermal conductivity with temperature was shown by aluminum, constantin, gold, manganin, palladium, platinum and tombac; and a decrease by bismuth, cadmium, iron, copper, lead, nickel, silver, steel and zinc.

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[1] J. D. Forbes, Athenäum, p. 1012, 1852.

[2] P. G. Tait, Trans. Roy. Soc. Edinb., p. 717, 1880; Phil. Mag. (5), 12, p. 147, 1881.

[3] A. C. Mitchell, Trans. Roy. Soc. Edinb., p. 435, 1887.

[4] W. Jäger u. H. Diesselhorst, Abh. d. Phys.-Techn. Reichsanstalt, 3, 269, 1900.

[5] L. Lorenz, Wied. Ann., 13, p. 422, 1881.

[6] T. C. Baillie, Trans. Roy. Soc. Edinb., 39, p. 361, 1897–98.

[7] F. Kohlrausch, Ztschr. f. Instruementk., 18, 139, 1898; Drude's Ann., 1, 145, 1900.

A New Method for the Determination of Thermal Conductivity.

In this investigation a new method, suggested by Professor C. E. Mendenhall, was used for the determination of thermal conductivity of metals at high temperatures. If a long cylindrical rod is heated electrically the temperature over a short distance *l*, symmetrically situated with respect to the ends, is approximately uniform and this approximation may be made as close as we please by increasing the length of the rod. In this central section, *l*, Fig. 1, the energy flow is then radial, *i. e.*, from the center to the circumference, and the quantity passing through any concentric cylindrical surface, of radius r and length l, is given by $-2\pi r l \lambda dT/dr$; where λ is the thermal conductivity and dT/dr the temperature gradient at r. When a steady state is reached we have

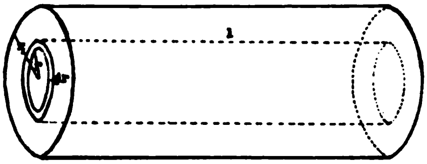

Fig. 1.

$$\pi r^2 l E I = -2\pi r l \lambda dT/dr;$$

integrating

$$\frac{EI}{2}\int_0^{r_1} r dr = -\lambda \int_{T_2}^{T_1} dT,$$

or

$$\lambda = \frac{E I r_1^2}{4(T_2 - T_1)}, \qquad (1)$$

where r_1 is the radius of the rod, E the fall of potential along one centimeter, I the current density, which is assumed constant over the cross-section and T_2 and T_1 are the temperatures at the center and circumference of the rod respectively. If the measurement of the fall of potential along l is difficult, as with alternating current, a separate determination of resistance at different temperatures may be made and IR substituted for E in the equation, R being the specific resistance.

The above discussion is on the assumption that the variation of specific resistance, due to the variation of temperature from inside to outside of the rod, may be neglected. As a closer approximation we may assume the radial variation of resistance to be proportional to r^2, as would follow to a first approximation from equation (1); substituting E/R for I we may write

$$R = R_2 - ar^2,$$

where R_2 is the resistance at the center of the rod. Then

$$\int_0^r \frac{E^2}{R_2 - ar^2} 2\pi r l dr = -2\pi r l \lambda dT/dr.$$

and

$$\frac{E^2}{2a} \log \frac{R_2 - ar^2}{R_2} = r\lambda dT/dr.$$

Dividing the equation by $E^2r/2a$ and integrating we obtain

$$\int_0^{r_1} \log\left(1 - \frac{a}{R_2}r^2\right)\frac{dr}{r} = \int_{T_1}^{T_2} \frac{2a}{E^2}\lambda dT$$

or

$$\lambda = \frac{E^2r_1^2}{R_2 4(T_2 - T_1)}\left[1 - \frac{ar_1^2}{4R_2} + \frac{a^2r_1^4}{9R_2^2}\cdots\right]. \qquad (2)$$

In this case the term outside the bracket is the value of λ obtained above. By substituting the values of a and R_2 as approximately known for any metal, the terms containing these quantities are seen to be negligible for rods less than 2 cm. in diameter.

For a hollow cylinder, where r_2 and r_1 are the inside and outside radii respectively, we have

$$\pi(r^2 - r_2^2)lEI = -2\pi r l \lambda dT/dr.$$

Integrating

$$-\lambda \int_{T_2}^{T_1} dT = \frac{EI}{2}\int_{r_2}^{r_1} (r^2 - r_2^2)\frac{dr}{r}$$

and

$$\lambda = \frac{EI}{2(T_2 - T_1)}\left[\frac{r_1^2 - r_2^2}{2} - r_2^2 \log\frac{r_1}{r_2}\right]. \qquad (3)$$

This is the formula used in the present investigation. As the energy is measured in watts, λ must be multiplied by .239 to reduce it to cal./cm. sec. degree.

When alternating current is used, these formulæ will not apply to magnetic substances as the "skin effect" must be considered in expressing the distribution of current inside the rod. The problem of determining thermal conductivity under these conditions was found too complicated for the present investigation and determinations on these substances were limited to temperatures such that the magnetic properties, as indicated by the presence of an appreciable skin effect, had disappeared.

Experimental Details.

The determination of thermal conductivity requires the measurement of three quantities: the dimensions of the rod, energy flow and temperature difference between the inside and outside of the rod.

1. *Dimensions of the Rod.*—Preliminary experiments showed that on heating a hollow rod six inches long the temperature was quite uniform over a length of one centimeter at the center. In order to decrease the heat flow to the ends of the rod the central hole was made larger at the ends and to within 1½ centimeters of the center; this increased the heat generated each side of the center by increasing the resistance and made the temperature uniform over a greater length. Determinations of temperature inside the rod at about 1000° C. showed a variation of approximately two per cent. over a length of two centimeters and less than one tenth of one per cent. over one centimeter. The measurement of temperature gradient did not require a uniform temperature over so great a length, but in the resistance determinations a uniform temperature was assumed over a length of one centimeter. The inside hole, .168 cm. in diameter, was drilled from each end and carefully reamed. In order to correct for any eccentricity, which might be present, temperature measurements were made at the ends of several radii in the central section. The outside diameter was approximately 1.2 cm., but varied slightly in the different determinations, due to polishing the surface. In order to eliminate oxidation the rod was enclosed symmetrically in a large, water-cooled cylinder from which the air could be exhausted.

2. *Energy Flow Measurements.*—As sufficient direct current was not available a welding transformer was used, capable of furnishing 1700 amperes at 2½ volts. The current was measured by means of a Weston ammeter accurate within one per cent. and a current transformer designed by Professor E. Bennett, of the engineering department of the university, accurate within one per cent. The measurement of low voltages with alternating current being unreliable a separate determination of the resistance at different temperatures was made, using direct current, and the resistance-temperature curve was plotted. For the resistance measurements the same rods were used as for thermal conductivity, with the outer diameter greatly reduced. The temperature for the resistance measurements was determined by a thermocouple in-

side the rod midway between the ends. The ammeter and voltmeter were calibrated in terms of laboratory standards. In order to eliminate the peltier effect at the point of contact of the potential terminals with the hot rod the terminals were made of fine wires of the same material as the rod; these being held parallel to each other and against the rod by brass frames. The distance between the terminals, approximately one centimeter, was measured by means of a micrometer gauge.

3. *Temperature Measurements.*—The temperatures were determined by two thermocouples, of No. 40 platinum and platinum-rhodium wire, standardized by using the boiling point of sulphur, the freezing point of antimony and the melting points of silver and gold. The electromotive forces of the thermocouples were measured on a potentiometer made for this work, the slide wire being one meter in length with six additional resistances each equal to that of the wire. One millimeter indicated 2 microvolts or about .2 degree and estimates were made to one tenth of this quantity. For small temperature differences the galvanometer deflections were also calibrated and could be estimated to one fifth of a microvolt or approximately .02 degree centigrade.

Measurement of Temperature Inside the Rod.—For the measurement of temperature inside the rod, the fine wires leading to the thermocouple were enclosed in small quartz tubes running longitudinally through the inside of the rod, with the junction itself midway between the ends. Breaking the quartz tube at the center appeared to make no difference in the temperature determinations.

Measurement of the Temperature of the Surface.—The greatest difficulty was to insure that the outer couple indicated the actual temperature of the surface; for this reason fine wires were used and, drawn diagonally

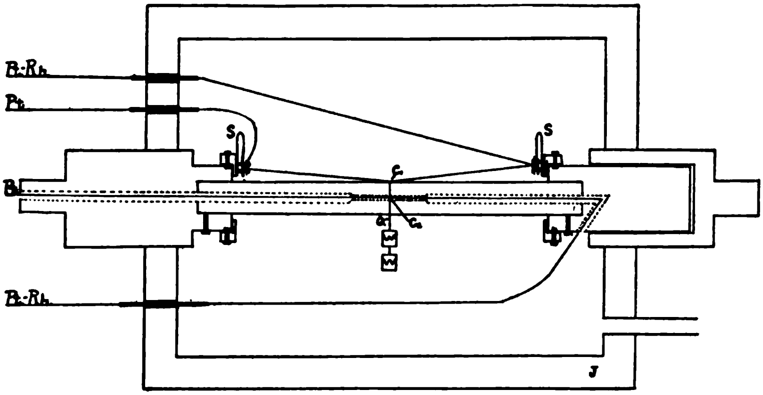

Fig. 2.

SS, springs; *CC*, thermocouples; *WW*, weights; *Q*, quartz fiber; *J*, water-jacket. Springs were rotated from position shown across the rod by two springs, were held close to the surface along its entire length (Fig. 2). The thermal junction was rolled in steel rolls to a thickness of .01 mm. and forced into contact with the highly polished surface by the small springs and by small weights hung over the rod by means of quartz fibers. A uniformly radiating surface in the neighborhood of the couple was found to be most important, so that either the rod must be platinum plated or the thermal junction covered with a layer of the same material as the rod. On account of the difficulty of platinum plating the second method was adopted; a piece of the same material as the rod was rolled in the form of a ribbon to a thickness of .01 mm. A short piece of this was then placed over the couple and held in contact with the rod by the quartz fibers and small weights, producing a uniform surface over the entire rod. Under these conditions the difference in temperature between the inside and outside of the rod was determined differentially at different temperatures and the curve plotted (Fig. 3, *A*); this curve could be repeated after rotating the outer couple around the rod, shifting slightly the inner couple or replacing the original couples by new ones from the same wire. The formation of a

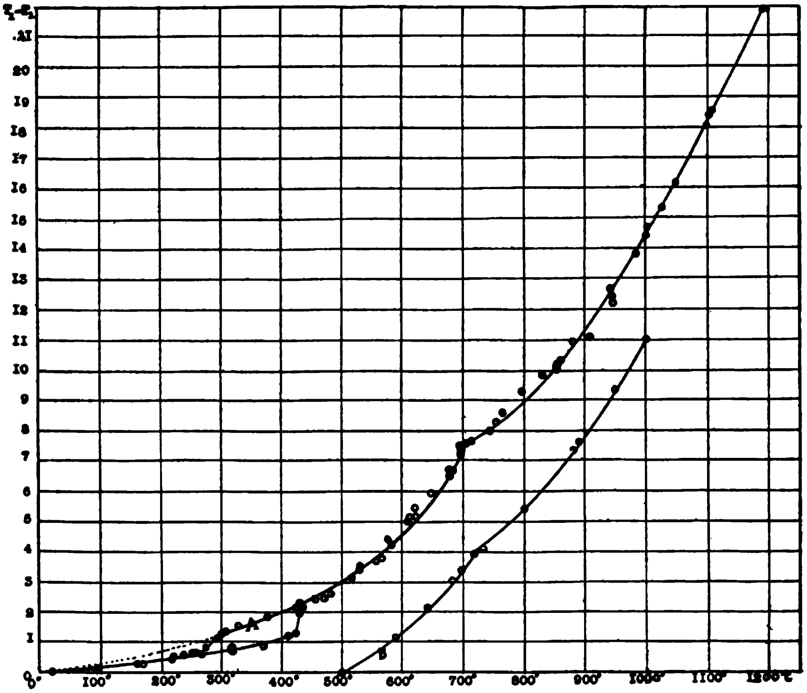

Fig. 3.

Variation of temperature-difference with temperature.

thin layer of oxide produced but small effect. The curve *B*, Fig. 3, of no value in the determination of thermal conductivity, was obtained when the nickel foil covering the couple was removed and the couple exposed. The platinum, being a poorer radiator than the nickel, acted as a shield at this point and the temperature was raised; below 500° C. the outer couple indicated a higher temperature than the inner. Poor contact between the outer ribbon and the rod was quickly indicated by the unsteady readings of the couple. In the work with nickel the dissociation temperature of nickel oxide was reached, due to the low pressure, at about 900° and the protecting ribbon was so completely welded to the rod that the two could not be distinguished. With the couple welded to the rod and imbedded under the surface to a depth of .01 mm. the quartz fibers were removed and the thermal conductivity curve determined with the rod rotated 120 degrees and 240 degrees from its original position. The agreement of curves indicated a symmetrical radiation from the surface of the rod in all directions. The rod was also heated when exposed to the air and a thick layer of oxide formed; under these conditions the temperature gradient was increased as the radiation from the surface was greater than before and temperature differences, for given inside temperatures, were greater than indicated by the curve (Fig. 3, *A*). There was, however, a corresponding increase in the energy required to maintain this temperature and the computed thermal conductivity curve coincided with that found when a bright surface was used. As criteria for deciding that the true value of thermal conductivity is obtained by this method we have, with a bright surface, the repetition of the temperature difference curve, on rotating the rod, rotating the thermocouple around the rod, displacing slightly the inner couple or on replacing the original couples by new ones from the same wire and the repetition of the thermal conductivity curve with a different radiating surface and therefore a different temperature gradient. Considering all the errors in measuring the dimensions of the rod, temperature, resistance and current, even when alternating current is used the error should be less than two per cent. above 300° C., while with direct current the error should not be over one per cent.

RESULTS. NICKEL.

Two rods of nickel from the same piece were used. This was obtained from H. Boker, New York, as the best available and no analysis has yet been made; probably however, it contains from two to three per cent of cobalt. The first rod was not heated above 700° C., and, within experimental error, gave the same temperature difference between the inside and outside, at a given inside temperature, for different positions of the couple around the rod and with the first couples replaced by new ones of the same wire. The second rod was of the same dimensions as the first and the curve showing temperature difference between the inside and outside of the rod for different temperatures coincided with that for the first rod and is shown in Fig. 3, *A*. The sharp rise in the curve at about 300° C. indicates the temperature at which nickel loses its magnetic properties; a change in the slope of the curve is also seen at about 700° C. From the electrical resistance at different temperatures, as shown in Fig. 4, the thermal conductivity at different temperatures

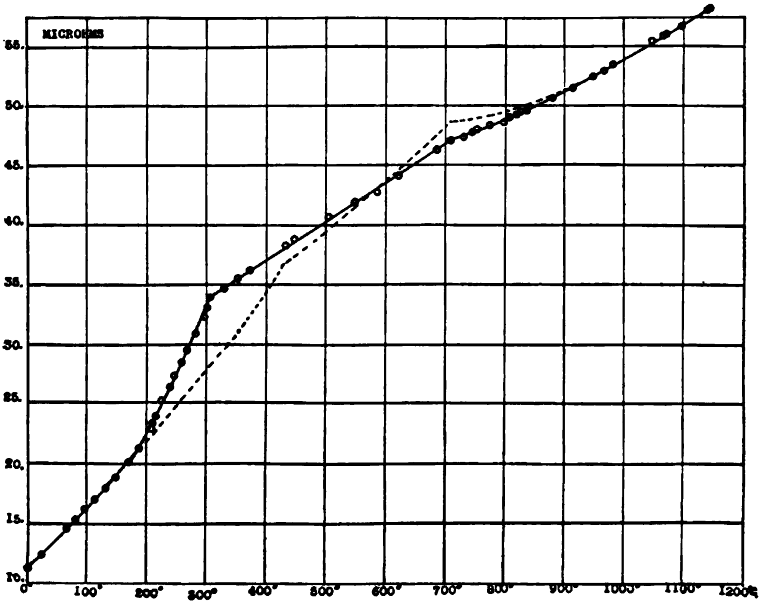

Fig. 4.

Resistance of nickel between 0° and 1200° C. The dotted line shows the resistance after sudden cooling; the full line, the resistance on first heating.

was computed and the curve drawn (Fig. 5). If this curve is prolonged to zero it will pass very nearly through the values of thermal conductivity given by Jäger and Diesselhorst, viz., .1420 at 18° C. and .1374 at 100° C. A prolongation of the curve may also be obtained by extending the temperature difference curve, shown by the dotted line in Fig. 3, *A*, as if undisturbed by skin effect and computing the thermal conductivity, at any temperature, from the current required to produce this temperature and the temperature difference determined from the curve. The second method is less reliable, however, as it does not allow for the fact that a greater amount of energy is required to produce a given inside temperature than if there were no skin effect. If the values of thermal conductivity found by Jäger and Diesselhorst at 18° C. and 100° C. are assumed for this specimen there is no change in the slope of the thermal conductivity curve at the temperature where nickel loses its magnetic properties, where, however, the change in the electrical conductivity is very marked. The thermal conductivity decreases more rapidly as the temperature increases up to 700° C., where its value is .069. At this point there is a most decided change in slope and the thermal conductivity decreases very slowly to 1225° C., with a value of .058 at this temperature. From the abrupt change in the slope of the curve one would conclude that an allotropic form of nickel is formed at about 700° C.

The temperature difference curve (Fig. 3, *A*) was repeated many times, and it was found that the readings did not check with the original curve between 300° C. and 420° C. after the rod had been suddenly cooled from high temperatures; the form of the new curve is shown by *C*, Fig. 3. Due to the sudden cooling the magnetic transformation point, as indicated by the sudden rise in the temperature difference curve, was changed from 310° C. to about 420° C. After annealing at about 900° C. and cooling very clowly to room temperature the transformation point was found at about 290° C., lower than at first. With this treatment it was possible to shift the transformation point at will between these limiting temperatures, 290° C. and 420° C.

As there is a decided change of slope in the electrical resistance curve at the magnetic transformation point the change in this curve was investigated when the transformation point was shifted; it had already been noticed that a smooth resistance curve could be passed through the points determined on the first heating of the rod, while those determined on cooling were not on this curve. The form of the curve as first determined and after sudden cooling is shown in Fig. 4, the transformation point being at 310° C. in the first case and approximately 420° C. in the second. With the transformation point between these limits the temperature-resistance curves were determined and when the transformation point was between 350° C. and 400° C., as assumed by Harrison[1] and Marvin,[2] the resistance between 0° C. and 350° C. could be approximately represented by a parabola. For a lower transformation point the form of the curve was shown by Knott[3] and is nearly a straight line up to 200° C. where the slope increases and continues nearly constant to the transformation point. Investigations of the magnetic properties of nickel by different observers have shown the transformation point to vary between 270° C. and 400° C.;[4] the lower values were commonly

[1] E. P. Harrison, Phil. Mag., June, 1904.

[2] C. F. Marvin, Phys. Rev., 30, p. 522, 1910.

[3] C. G. Knott, Trans. Roy. Soc. Edinb., p. 33, 1888.

[4] Honda and Shimizu, Phil. Mag., Oct., 1903.

supposed to be due to impurities, but from this work appear to depend more upon the treatment of the specimen. The probable explanation of the fact that different observers have not obtained more nearly the same magnetic transformation point is the lack of annealing at a sufficiently high temperature.

It is customary to associate a change in the properties of a substance with a change in molecular structure and metallurgists have found an alpha, beta, gamma and even a delta state for iron and an alpha and beta state for nickel, but I believe this is the first indication of a third allotropic form, "gamma," for nickel, which appears at about 700° C. The change in the thermal conductivity curve at this temperature is very decided, as is shown in Fig. 5; the change in the resistance curve is not marked when the transformation point is in the neighborhood of 300° C., but with the transformation point at 420° C. a decided change of slope is observed. In the resistance curve given by Sommerville,[1] this change of slope is not apparent, but in a later paper[2] where the slope of the curve is given the change is plainly shown. Apparently there is a molecular rearrangement at about 700° C., producing an allotropic form of nickel, which is carried down by quenching and causes a change in the resistance and magnetic properties.

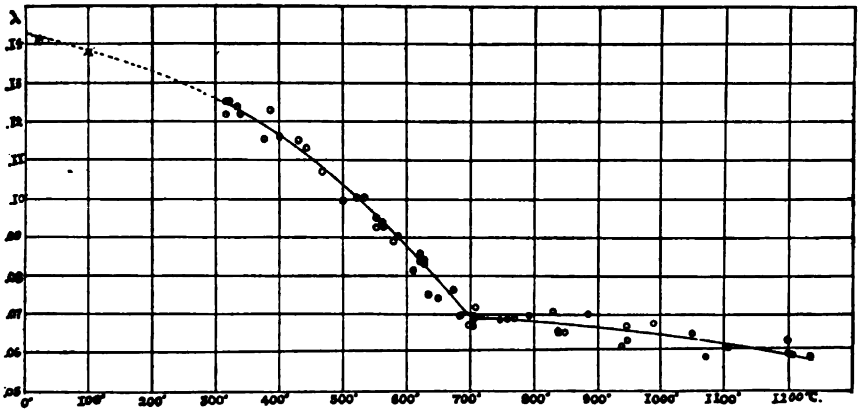

Fig. 5.

Thermal conductivity of nickel, 300°–1200° C. × ×, values of Jäger and Diesselhorst.

In order to compare the elasticity under different conditions a test was made with a Shore scleroscope, by measuring the rebound of a small hammer dropped upon the specimen; using the same rod as for the electrical and thermal conductivity experiments, the rebound was found to be much less after quenching, in the ratio of 7.2 to 14.

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[1] A. A. Sommerville, Phys. Rev., 30, p. 532, 1910.

[2] A. A. Sommerville, Phys. Rev., 31, p. 261, 1910.

ALUMINUM.

A single aluminum rod, of the best commerical grade, 99 per cent. pure, was tested. The determination of thermal conductivity, shown in Fig. 6, was less satisfactory than with nickel, on account of the low electrical resistance and high thermal conductivity, which increases with temperature; both of these properties tending to decrease the temperature difference between the inside and outside of the rod. The determinations near 100° C. agree well, however, with the value .492, which was found by Jäger and Diesselhorst at this temperature and their values were used to prolong the curve to zero. Their values may be assumed for this specimen as the purity of the aluminum was about the same in both cases. The thermal conductivity of aluminum increases more rapidly at high temperatures than between 18° C. and 100° C., increasing from .49 at 100° C. to 1.0 at about 600° C.

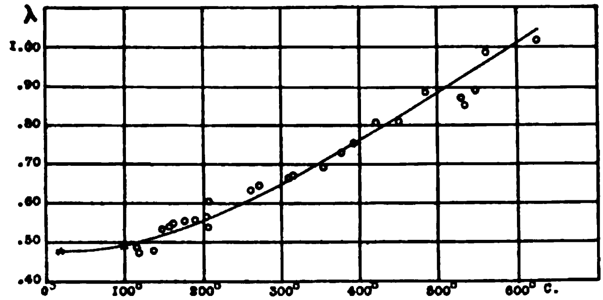

Fig. 6.

Thermal conductivity of aluminum. × ×, values of Jäger and Diesselhorst.

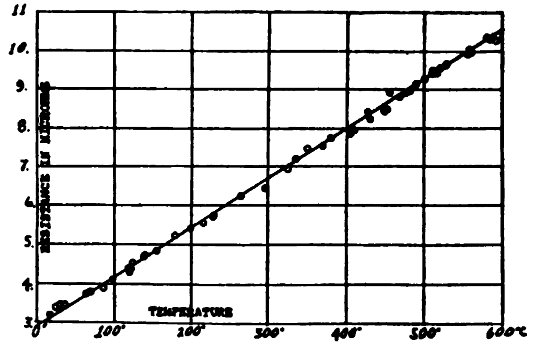

Fig. 7.

Resistance of aluminum.

In order to insure good contact with aluminum, where the protecting strip could not be welded to the rod, a small weight with a very sharp point was dropped repeatedly upon this outer strip and very fine holes made into the rod, then with a small hammer the strip was pounded down tight and smooth over the surface. By this method very many small portions of the outer strip were forced into the holes in the rod and the strip held in close contact.

The electrical resistance curve (Fig. 7) coincides very closely with that given by Sommerville[1] for a good grade of commercial aluminum.

SUMMARY.

1. A new method of determining thermal conductivity has been tried and shown practicable with metals at high temperatures.

2. The thermal conductivity of nickel, between 300° C. and 1200° C. and of aluminum between 100° C. and 600° C. has been determined.

3. There is no constant ratio between electrical and thermal conductivities for these metals at high temperatures. At high temperatures the thermal conductivity of aluminum increases, and of nickel up to 700° C. decreases, more rapidly than from 0° C. to 100° C.; above 700° C. the thermal conductivity of nickel decreases very slowly up to 1225° C.

4. A third allotropic state for nickel has been found at about 700° C., with a change in the form of the electrical and thermal conductivity curves at this point.

5. The magnetic critical temperature of nickel has been shown to be shifted through a range of one hundred and thirty degrees by heat treatment; annealing from high temperatures giving a low value and sudden cooling producing values as high as 420° C.

6. The electrical resistance of nickel between 0° C. and 1200° C. and of aluminum between 0° C. and 600° C. has been found and, for nickel, the change in the form of the curve which accompanies a change in the magnetic critical temperature due to heat treatment has been determined. It was found that the temperature-resistance curve could be approximated by a parabola only when the critical temperature was in the neighborhood of 370° C.

7. The elasticity of nickel was greatly reduced by quenching, but could be increased to its original value by annealing at high temperatures.

In conclusion I wish to express my most sincere thanks to Professor Snow for placing the necessary apparatus at my disposal and to Professors Mendenhall and Mason for their kindly interest and helpful suggestions throughout this investigation.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
July, 1911.

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[1] A. A. Sommerville, PHYS. REV., 31, p. 261, 1910.

ON THE FATIGUE OF METALS SUBJECTED TO ROENTGEN RADIATION, IN THE PRESENCE OF CHEMICALLY ACTIVE GASES.

By Edward G. Rieman.

THE recent experiments by Professor More[1] and Dr. Gowdy,[2] show that metals, subjected to Roentgen radiation, suffer changes of secondary radiation, in a manner somewhat similar to that found by Hallwachs[3] in the case of metals acted upon by ultraviolet light. This action has been designated by the term fatigue.

For example, it was found that a freshly polished iron disk, when exposed to X-rays, in an atmosphere of air, gave after three hours exposure, a secondary radiation which was four per cent. greater than the original. On the other hand, a disk of lead exposed for the same length of time, under the same conditions, showed a decrease in secondary radiation of three per cent.

Furthermore, it was found that chemical change of the surface was necessary in order to have fatigue take place. Metals exposed in the inactive gas, carbon dioxide, showed no fatigue. Disks whose surfaces were old and chemically stable gave no fatigue when experimented upon in an atmosphere of air.

As the above authors have worked only with air and ozone, both of which form oxides on the surfaces of metals, it is desirable to study the effects which occur in atmospheres of other chemically active gases and vapors.

Practically the same apparatus and methods were employed in the following experiments as were used by Dr. Gowdy. A brief description of these can be given as follows:

The X-ray tube, T, which can be rotated about a vertical axis is contained in a large lead-covered box. Two thick brass tubes, P_1 and P_2, direct the rays into two similar cubical ionization chambers. An aluminum gauze, G, is supported by ebonite insulators and is held firm at a distance of one centimeter from the disk holder, H. This holder is designed to carry the disk and is held in place by the sulphur plug, S. Highly insulated and metallically shielded wires connect the holders to the Wilson electroscope, *E*. The two gauzes are maintained at opposite potentials of 80 volts, this being sufficient to produce saturation. The process of taking readings was as follows.

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[1] More, Phil. Mag., XIII., p. 708.

[2] Gowdy, Phys. Rev., Jan., 1910, p. 62.

[3] Hallwachs, Sitzungsbericht der Ges. der Wissensch. zu Leipzig, LVIII., 1906, p. 341.

Two disks of the same metal, one called the standard and the other, the trial plate, were placed in the holders. By rotating the X-ray tube, the radiation falling upon the disks was adjusted so as to make the two currents set up in the ionization chambers exactly equal; this balance could be recognized when no deflection of the electroscope occurred. When the balance had been obtained, electrical connection between the electroscope and the holder of the trial plate was broken by means of the switch, *W*, and a time deflection reading, called, t_1, was taken in order to get a quantity proportional to the amount of secondary radiation given off by the standard plate. Owing to the existing electrical balance, this amount was also necessarily equal to the amount given off by the trial plate. Several readings for both plates showed this to be the case.

The standard plate was then shielded while the other remained exposed to the X-rays. At intervals of an hour, trials were made to see whether or not the balance still existed; if it persisted, both plates were evidently still giving off equal amounts of secondary radiation However, if the balance were destroyed, a time deflection reading, t_d, was taken, and this reading served to indicate the increase or decrease of secondary radiation given off by the trial plate. A substitution of the readings, t_1 and t_d, in the formula developed by Dr. Gowdy gave the percentage fatigue suffered by the exposed plate.

For further details reference may be made to the papers cited.

Although this balance method is in itself accurate, certain refinements in the method of taking readings have been adopted for the following experiments. It is evident, that a true reading for fatigue can only be taken when the following conditions are fulfilled. First, the specific ionization of the atmosphere in which the readings are taken, must be the same for every observation. Second, the primary radiation falling upon the disks, for each subsequent reading, should be equal to that for the first reading, t_1.

The first of these conditions was obtained by taking all observations when the disks were in an atmosphere of dry air; no other gas being permitted in the ionization chambers. The bombardment of the plates by the X-rays, and their fatigue occurred in a specially constructed box which was so arranged, that while both plates were subject to the action of the chemically active vapor or gas, the trial plate alone was exposed to the X-rays. Thus, any change in sensitiveness, which would be caused by the exposure to the vapor itself, would be balanced; since both plates suffered a like amount, and the fatigue noted in the observations, would be due entirely to the action of the Roentgen rays upon the trial plate.

In order to be certain that the primary radiation falling upon the disks was the same for every reading the following method was resorted to. After the original balance at the start of any series of readings had been established and the reading, t_1, taken, the disks were removed quickly from the holders and placed in the bombarding chamber. Readings were then taken to give the amount of secondary radiation for each of the holders. Thus the above mentioned second condition of refinement could be fulfilled, by simply adjusting the X-ray tube until the readings for secondary radiation from the holders, with the disks removed, were duplicated. This was, as a rule, easily accomplished and made every reading valuable.

In order to reduce possible irregularities, such as arise from a prolonged operation of the coil and tube, two sets of coils and tubes were used. One of these could be employed to fatigue the disks, which requires no absolute regularity, and the other be kept in reserve for accurate measurements.

Oxygen, chlorine, bromine, hydrogen sulphide, nitric acid and hydrochloric acid were the gases and fumes with which experiments were tried. Carbon-dioxide, which is inactive, and in the presence of which no fatigue occurs, served as a dilutent for these other highly active chemical agents. Experiments were also tried with mixtures varying in the percentage of carbon dioxide. All gases before entering the exposure chamber were carefully purified and dried.

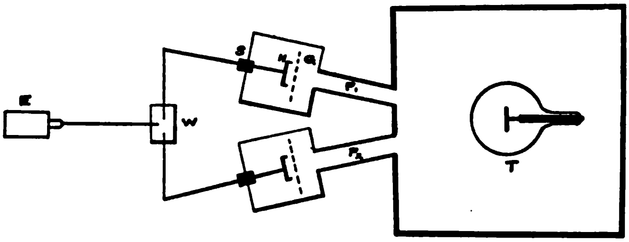

Fig. 1.

Table I. shows results for fatigue occurring in an atmosphere of almost pure oxygen; Table II. the results when about 50 per cent. carbon dioxide was present. The figures represent the percentage of radiation given off, by the fatigue plates, where 100 indicates the initial amount. In Table I., the values are the average of from two to four different series of exposures while those in Table II. are single readings.

Table I.

Fresh Surfaces in Pure Oxygen.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0	100.0−	100.0	100.0−	100.0−	100.0
2	100.0+	99.5−	100.0−	99.0−	99.5	100.0−
3	100.5+	99.0−	99.0−	98.0+	99.0+	99.5+
4	100.5+	99.5	99.0−	98.5−	98.5−	100.0−
5	101.0+	98.5+	99.0+	97.5	99.0−	100.0−
6	102.0+	98.5+	98.0+	96.0+	98.0−	100.0
7	101.5	—	—	—	98.0	—
8	—	98.0−	—	97.0	—	100.0−
9	102.0+	—	99.0−	97.5−	—	—

Table II.

Fresh Surfaces in Oxygen and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0	100.0−	100.0−	99.5−	100.0	—
2	100.0	100.0−	99.0+	99.5	100.0	—
3	100.0+	99.0+	99.0	98.0−	—	—
4	100.5	98.5+	99.0+	98.5−	99.0	—
5	101.5	99.0−	98.5−	—	97.5+	—
6	101.5−	99.0−	—	96.0−	—	—
7	—	98.5+	—	—	98.5−	100.0−
8	102.0+	—	98.5+	—	—	—
9	102.5−	99.0−	—	97.0−	—	100.0−

The formation of an iridescent film was noted in the case of the exposed copper disk. This film was always more noticeable on the days following the exposure, so the chemical action apparently persisted after the experiment. A film also formed on the standard copper plate causing it to appear dull in comparison to the other. Iron and lead also showed a small film action.

Table III.

Aged Surface in Chlorine and CO_2 Mixture.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0−	100.0	100.0	100.0−	100.0−	100.0
2	100.0−	100.0−	100.0+	99.0+	—	100.0
3	100.0−	100.0+	99.0+	98.0	99.0−	100.0+
4	99.5−	99.0−	100.0−	99.0−	—	—
5	99.5+	99.5	—	—	97.5−	100.0+
6	99.0+	—	100.5−	—	96.5+	100.5−
7	98.5	98.5−	—	97.5−	—	101.0−
8	99.0−	—	100.5+	97.0−	97.5	—
9	99.0−	97.0+	—	—	—	100.5+

TABLE IV.

Freshly Polished Surfaces in Cl and CO_2 Mixture.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0−	100.0	99.0+	100.0−	100.0−	100.0
2	100.0−	99.0+	99.0−	99.0−	99.5−	100.0−
3	99.5+	98.5−	98.0−	98.0−	99.5−	——
4	99.5+	97.5	98.0	98.0+	99.0+	100.0−
5	99.0+	97.0−	98.5−	96.5	——	100.0
6	100.0−	98.0−	——	96.0−	97.0+	100.0+
7	100.0−	98.0−	98.5−	——	98.0−	100.0+
8	99.0	——	——	97.5	——	100.0−
9	99.5−	——	——	——	98.0+	100.0

Table III. shows the results when an old oxide coated surface, five to six days old, suffers fatigue in an atmosphere of chlorine and carbon dioxide; Table IV., the observations for freshly polished surfaces. In comparing the readings for iron on the two tables, it is curious to note that the old stable surface suffered a fatigue equal to one and a half per cent., while the freshly polished iron disks showed only a slight fatigue. It is possible to explain this if we remember, that in the case of an old stable oxide surface, oxidation and its accompanying increase of secondary radiation is not likely to take place. In the case of a freshly polished disk, enough air might cling to the newly formed chloride surfaces during the transfers to and from the ionization chambers, to cause an oxygen fatigue to take place along with the chlorine, and thus retard the decrease of sensitiveness due to the action of chlorine. That something of this nature must occur will be shown by the results of later experiments. According to Table III. tin and aluminum suffered an increase of sensitiveness. This was the only case in which aluminum showed any decided fatigue. Experiments were also tried for mixtures containing different percentages of chlorine. The results were practically the same as those given and were therefore not tabulated.

TABLE V.

Long Exposure in Cl and CO_2 Mixture.

Hours.	Fe.	Fe.	Fe.	Zn.	Zn.	Zn.
6	——	——	——	98.0	——	——
7	99.0−	——	——	——	——	——
8	——	98.0−	——	——	——	98.5+
9	99.0−	——	98.5−	98.5	98.0+	97.5−

Table V. shows the readings taken for freshly polished iron and zinc disks, which were allowed to remain in the exposure chamber six hours or more, before observations were taken. In this way any oxidation due to the air in the ionization chambers was avoided. In the case of iron we see that the fatigue is decidedly greater than that given in Table IV. The fatigue for zinc was practically the same as is given in the former table.

Table VI.

Freshly Polished Iron in Chlorine and Oxygen Mixtures.

Hours.	5 Per Cent. Cl. Spec. I.	15 Per Cent. Cl. Spec. II.	20 Per Cent. Cl. Spec. III.
1	100.0	——	100.5
2	100.0	100.0	100.0+
3	——	99.5−	100.0
4	99.5+	99.5−	99.5+
5	100.0+	99.0	——
6	100.0−	99.5−	——
7	100.0−	——	99.5+

Table VII.

Disks Previously Exposed to Cl and O, in Nitric Acid.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0−	100.0	100.0	100.0−	99.5−	100.0
2	100.0−	100.0	100.0	99.5	99.0−	100.0−
3	99.5−	100.0−	——	——	——	——
4	99.0+	100.0−	100.0−	99.0+	99.5−	100.0−
5	99.5−	——	——	98.0−	——	100.0
6	——	——	——	98.5−	98.5+	——
7	——	99.5−	100.0−	——	——	100.0
8	——	——	——	——	97.0−	——
9	——	99.0	——	99.0−	——	——

Table VIII.

Fresh Surfaces in Nitric Acid.

Hours.	Fe.	Cu.	Sn.	Pb.	Sn.
1	100.0−	99.0−	——	99.5−	99.0−
2	100.0−	98.0−	——	99.5+	99.0−
3	100.0−	97.0+	——	——	——
4	99.5−	97.5	99.0+	99.5	99.5
5	99.0−	97.0+	——	99.0	99.5−
6	99.5−	96.0−	100.0−	——	99.0+
7	99.0	96.0−	100.0+	99.0−	——
8	——	——	——	98.0−	98.5−
9	98.0−	——	——	——	——

Table VI., which shows the results for three series of readings taken for mixtures of oxygen and chlorine, indicates that hardly any fatigue takes place in this atmosphere. Mixtures varying in chlorine from five to twenty per cent. were used. This table substantiates the former proposed theory, namely that for a mixture of two chemically active gases a double fatigue may take place. In this case the oxygen by Table I. would cause an increase in sensitiveness while the chlorine according to Table V. a decrease. The two fatigues occurring at the same time would counteract each other and hence no change of sensitiveness would be noted.

The readings in Table VII. give the fatigue of metals which had previously suffered exposure in both chlorine and oxygen, and were then fatigued in an atmosphere of carbon dioxide and nitric acid fumes. The lead and zinc disks, although thickly coated with films due to the chlorine and oxygen, show a decided change of sensitiveness.

Table VIII. gives the results for freshly polished disks fatigued in an atmosphere of carbon dioxide which had passed over fuming nitric acid. Copper showed a very noticeable fatigue and also a decided film action.

Table IX.

Fresh Surfaces in Bromine and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0	100.0 –	——	100.0 –	100.0	100.0
2	100.0	100.0 –	100.0 –	99.5	100.0	100.0 –
3	100.0 –	100.0 –	99.5 –	99.5 –	——	——
4	100.0 –	——	——	99.5 –	100.0 –	——
5	——	99.5 –	100.0 –	——	——	——
6	100.0 +	——	99.0 –	99.0 +	100.0 –	100.0 –
7	——	99.5 –	98.5 –	——	100.0 –	——
8						
9						

Table X.

Fresh Surfaces in HCl Fumes and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.
1	100	100	100.0	100.0	100.0
2	100	——	99.0 –	100.0	100.0 –
3	99.5	99.0 –	99.5 –	99.5 +	99.5 –
4	99.5 –	98.0 –	99.5 –	99.5 +	99.5 –
5	——	98.0	98.5	100.0 –	——
6	99.0 +	96.5 –	98.0 –	99.0 +	
7	99.5	96.0	98.0 –	——	99.0
8	——	96.5 –	——	99.5 –	——
9	——	——	97.0 –	——	99.5 –

Tables IX. and X. give the fatigue for disks with fresh surfaces, exposed in bromine vapor and CO_2. While bromine caused a decided film action, hardly any fatigue was noted except in the case of tin. The fatigue occurring in hydrochloric acid fumes was about equal to that for chlorine gas, copper giving a slightly greater change for the fumes.

TABLE XI.

HCl Coated Disks in Hydrogen Sulphide and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.
1	100.0	100.0	100.0−	99.5	100.0
2	100.0	100.0−	100.0—	99.0−	100.0
3	100.0−	98.5	100.0−	——	99.0+
4	100.0	99.0+	99.5−	98.0−	98.5−
5	100.5+	99.5−	98.5−	97.5+	99.0
6	100.0	98.5	98.0	96.5	——
7	——	98.0	98.0	98.5+	——
8					
9					

TABLE XII.

Freshly Polished Disks in H_2S *and* CO_2.

Hours.	Fe.	Cu.	Pb.	Zn.
1	100.0	100.0	100.0	99.0+
2	100.0	100.0	99.5−	98.0−
3	100.5+	100.0	98.0−	98.0−
4	100.5	98.5+	96.5−	98.0−
5	——	98.0−	95.0	——
6	101.0+	97.0	95.0−	——
7	101.0+	97.5−	95.0−	98.0+
8	——	98.5−	94.5−	——
9				

Tables XI. and XII. show results for exposure occurring in atmospheres of H_2S and CO_2. Freshly polished lead, immersed in hydrogen sulphide, gave the greatest fatigue of any metal in any gas. The readings given for lead are the averages of three series of observations. The film action for hydrogen sulphide was very noticeable for every metal.

SUMMARY OF RESULTS.

Fatigue occurred when freshly polished surfaces of iron, copper, tin, lead, and zinc were exposed to X-rays, in the presence of oxygen or a mixture of oxygen and carbon dioxide. Aluminum showed no appreciable change. The fatigue for metals exposed in an atmosphere of pure oxygen was practically equal to that which occurred when fifty per cent.

CO_2 was present. It was also found that the changes in secondary radiation of all metals in chlorine and CO_2 were pratically of the same amount, although the percentage of the mixture was varied through rather wide limits.

Old oxide surfaces, which are stable so far as fatigue in an atmosphere of oxygen is concerned, showed decided fatigue when tested in chlorine.

In the case of iron exposed in an atmosphere of chlorine and oxygen, a double fatigue seemed to take place, one tending to increase and the other to decrease the radiation.

Fatigue was found for metals with freshly polished surfaces when exposed in chlorine, bromine, nitric acid fumes, hydrogen sulphide, and hydrochloric acid. In some cases, surfaces which had undergone a previous chemical combination, showed a further combination and fatigue when exposed to another chemical agent and the X-rays.

No relation has been found between the amount of fatigue for a metal and the corresponding activity of chemical action of the gas and the metal.

In conclusion I wish to extend to Professor More my sincere thanks for his advice and many suggestions during this work and also acknowledge the assistance rendered by the grant from the Bache Fund of the National Academy of Sciences.

University of Cincinnati,
June, 1911.

NEW RECORDS OF SOUND WAVES FROM A VIBRATING FLAME.

By Joseph G. Brown.

VIBRATING flames are commonly classified as singing flames sensitive flames, and manometric flames. The singing flame was first observed by Higgins[1] in 1777, soon after the discovery of hydrogen. The term singing flame is now usually limited to flames which vibrate in a pipe or other resonator. The sensitive flame was first observed by LeConte[2] in 1858, and any naked flame which vibrates under the action of sound waves is termed sensitive. In 1862 Koenig[3] devised his manometric capsule, and he called the flame which was made to vibrate by means of the capsule a manometric flame.

In the study of vibrating flames two distinct optical methods have been employed. The method of the revolving mirror was first applied by Wheatstone[4] in 1834 to the singing flame. Tyndall,[5] Barrett,[6] and others made observations by this method upon both the singing and sensitive flames.

The stroboscopic method of observation was devised by Toepler[7] in 1866. As a means of examining the action of the vibrating flame this method is unsurpassed; because the different phases of the vibration may be observed and studied at will, and made to succeed each other at any desired rate.

Flame Pictures.

When Koenig devised his manometric flame he used the revolving mirror method of observation and called the view which he thus obtained a flame picture. In his attempt to analyze the vowel sounds, Koenig[8] sketched a number of these flame pictures. Later, the flame pictures were photographed by Doumer,[9] Merritt,[10] Hallock,[11] Nichols and Merritt,[12] and Austin.[13]

It is very evident that the flame pictures are in no sense time-displacement diagrams of the sound waves producing them. They are overlapping images of successive phases of the vibrating flame, and the wave form can only be inferred approximately from such a result. The luminous tip of the vibrating flame is not a definite thing which vibrates vertically. The stroboscopic observations of Toepler[1] and the photographs of Marbe and Seddig[2] show that the flame consists of alternating expansions and contractions which continually move upward and burn out as they rise. The expansions are much brighter than the contractions and often are the only luminous parts of the flame. If the variations in pressure are quite small as compared with the mean pressure of the gas, the shape of the flame changes very little and the tip executes a vertical vibration. In this case, the flame picture approaches a time-displacement diagram, but the distortion due to the upward moving enlargements and contractions is always noticeable. If the variations in pressure are large, the change in shape of the flame is very marked, the tip becoming mushroom shaped. Or if the change in pressure is large and sudden, a vortex ring is formed which separates entirely from the main body of the flame.

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[1] Nicholson's Jour., 1, 129, 1802.

[2] Am. Jour. of Sci., 75, 62, 1858.

[3] Pogg. Ann., 122, 242, 1864.

[4] Phil. Trans., 1834, p. 586.

[5] Phil. Mag. (4), 13, 473, 1857.

[6] Phil. Mag. (4), 33, 26, 1867.

[7] Pogg. Ann., 128, 126, 1866.

[8] Phil. Mag. (4), 45, 1 and 105, 1873.

[9] Phil. Mag. (5), 22, 309, 1886.

[10] Phys. Rev., 1, 166, 1893.

[11] Phys. Rev. 2, 305, 1895.

[12] Phys. Rev., 7, 93, 1898.

[13] Phys. Rev., 12, 121, 1901.

On account of this complicated action of the vibrating flame, the flame pictures have never been very successful as a means of analyzing sound waves. Some time ago it occurred to me that certain modifications in the flame and in the method of making observations, might result in obtaining a time-displacement diagram which would give the wave form with considerable accuracy. The chief object of this paper is to describe some attempts which I have made with this object in view, and to present some of the records obtained.

My plan has been to vibrate a flame with sound waves of known form and then to modify the conditions until the wave form was obtained. The sound wave from a telephone receiver vibrated by the alternating current of the lighting circuit, was used as a standard source for all preliminary trials. The arrangement was very similar to that used by Austin,[3] and later by Marbe.[4] The oscillograph record of this circuit was extremely close to a sine curve, and the vibration of the telephone disc, when tested by the method of D. C. Miller,[5] was found to be almost simple harmonic.

SMOKE RECORDS.

The first modification which I tried suggested itself to me while I was repeating the smoke ring experiment of Marbe.[6] This consisted in projecting the jet tube at a considerable angle away from the vertical, keeping it perpendicular to the direction of motion of the paper, and allowing the tip of the smoky acetylene flame to come in contact with the paper. My idea in doing this was that the variations in pressure which tend to lengthen and shorten the flame might give the tip a transverse vibration which would be indicated by the deposit of soot. I soon found that with proper adjustment of the jet the soot was deposited upon the paper in lines and bands. (See Fig. 1.) A very fine line (*a*) was formed by a thread of soot which appeared to come from the center of the flame. A coarser line (*b*) was formed by a thread of soot which came from the forward side of the flame; *i. e.*, from the side in the direction in which the paper was moving. A similar thread came from the backward side of the flame, but it was not deposited upon the paper. A heavy, narrow band of soot (*c*) was deposited from the near side of the flame; *i. e.*, from the side nearest the jet; and a light, broad band (*d*) came from the far side of the flame. This result was obtained with a jet tube having an opening about 1 mm. in diameter, projected about 65° away from the vertical, with the opening about 2 cm. from the paper, and with a gas pressure of about 2 mm. of water. The paper was in the form of a belt upon two brass drums. One drum was rotated by an electric motor and the flame was placed under the other drum. The paper moved past the flame with a velocity of about 75 cm. per second. When the flame was vibrated by the telephone receiver the lines and bands of soot were deposited as shown in the right half of Fig. 1. It will be noticed that the fine line (*a*) indicates only the longitudinal vibration of the flame and comes the nearest to being a sine curve, hence represents most nearly the form of the sound wave. The coarse line (*b*) indicates the longitudinal vibration of the flame fairly well but it is not a sine curve, the distortion being due to the expansions and contractions of the flame. This distortion might be expected from the fact that this line is deposited from the edge of the flame, while the fine line is deposited from the center of the flame. The narrow band (*c*) shows the longitudinal vibrations to some extent, but on account of the transverse vibration the soot from the band is deposited heavier on certain areas when the relative velocity between the edge of the flame and the paper is small, and lighter on other areas when the relative velocity is large. This produces an interesting pattern which characterizes the vibration but is difficult of interpretation. The broad band of soot (*d*) shows this effect of the transverse vibration to a marked extent. I am inclined to think that the formation of the rings observed by Marbe is explained in the same way.

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[1] Loc. cit.

[2] Wied. Ann. (4), 30, 579, 1909.

[3] Loc. cit.

[4] Phys. Zeit., 7, 543, 1906.

[5] PHYS. REV., 28, 151, 1909.

[6] Loc. cit.

Unfortunately the fine line does not stand out by itself but is partly

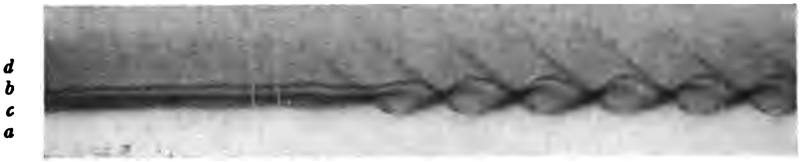


Fig. 1.

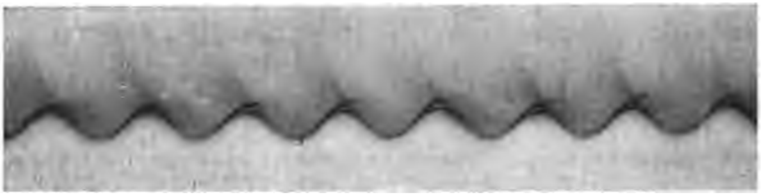


Fig. 2.

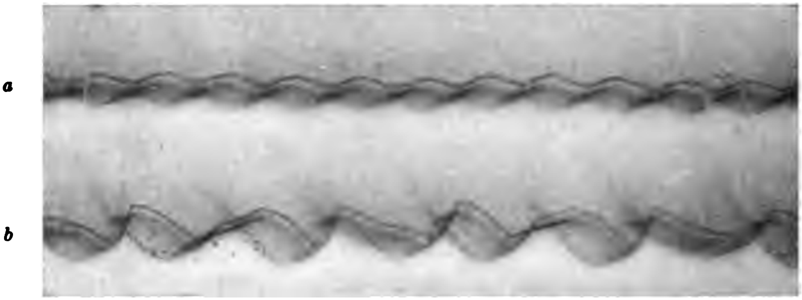


Fig. 3.

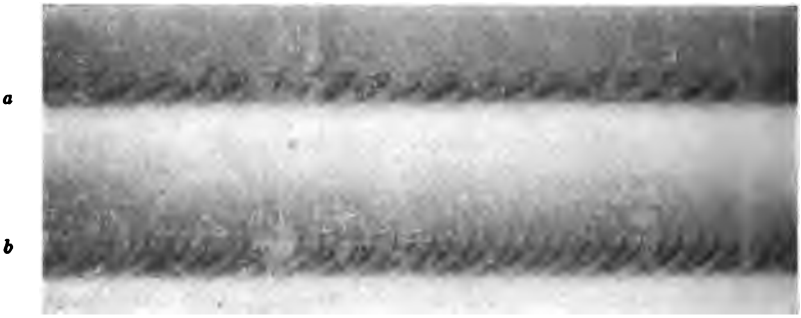


Fig. 4.

F. G. BROWN.

PLATE I.

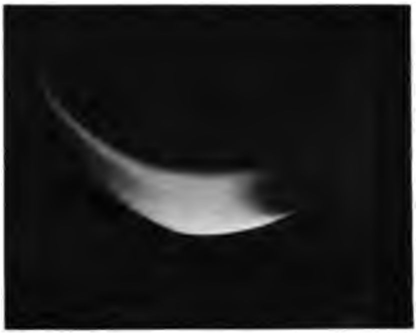


Fig. 5.

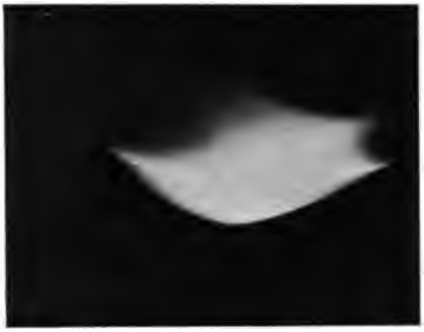
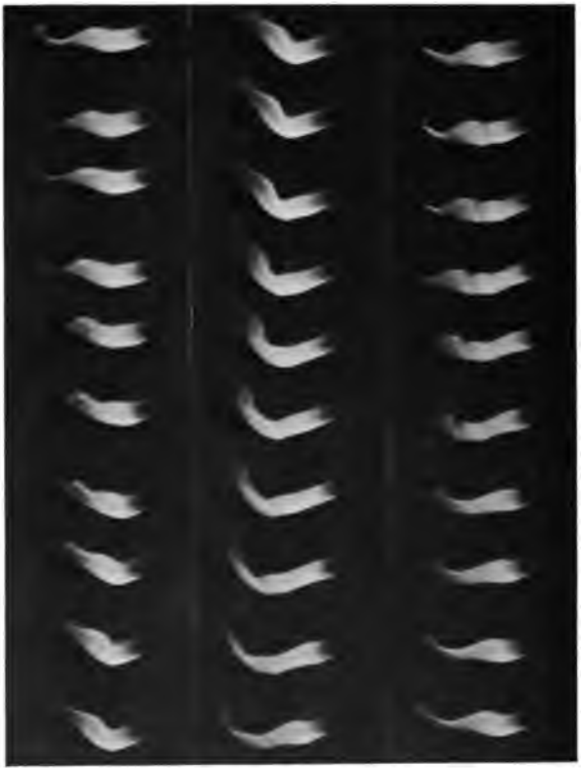


Fig. 6.



a *b* *c*

Fig. 7.

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PLATE II.

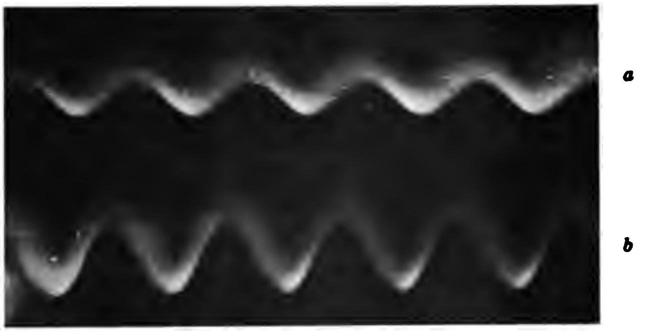

Fig. 8.

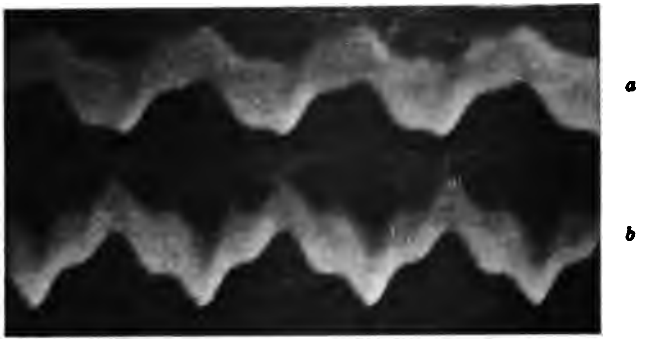

Fig. 9.

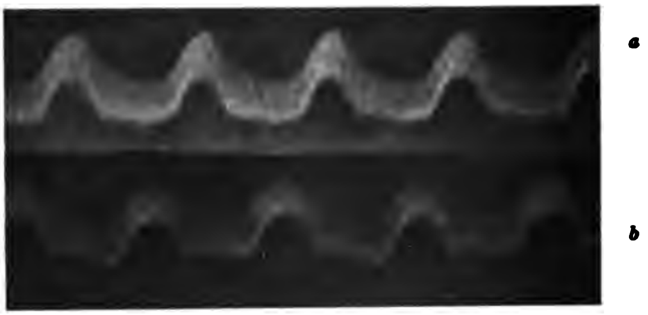

Fig. 10.

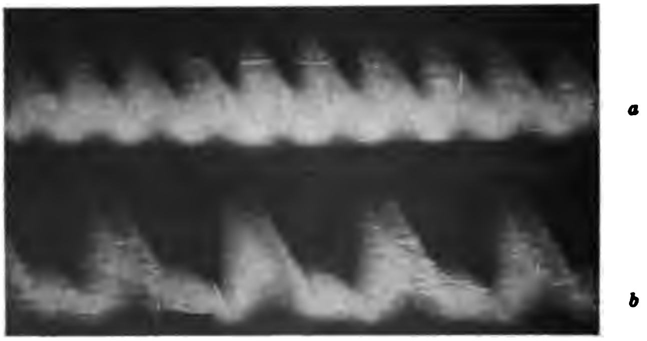

Fig. 11.

F. G. BROWN.

Plate III.

covered by soot from the other sources. This can be avoided by using a greater gas pressure and consequently a larger flame, but the sensitiveness is greatly reduced. Fig. 2 shows the result of this adjustment.

A few records from other sources will serve to show the extent to which this method will reproduce complicated wave forms. The smoke record of an electrically vibrated tuning fork ($n = 100$) placed in front of a Koenig capsule, is shown in Fig. 3 (*a*). The result of the composition of this fork with the alternating current ($n = 61$) is shown in Fig. 3 (*b*). A record of sung vowels is shown in Fig. 4; (*a*) is "e" as in "he," and (*b*) is "a" as in "hay."

PHOTOGRAPHIC RECORDS.

The second modification was suggested by the fact that the lower luminous edge of the projected flame seemed to be exceedingly sharp and to vibrate with considerable amplitude. This was especially noticeable when the jet tube was projected about 45° below the horizontal and a small quantity of illuminating gas was mixed with the acetylene to keep the flame from smoking. Fig. 5 is a photograph of such a flame when steady, and Fig. 6 is the same flame while being vibrated by the alternating current. When this vibrating flame was examined with a stroboscope, it was very evident that the longitudinal vibration at the base of the flame was very largely carried over into a transverse vibration of the luminous part of the flame. This is strikingly shown by a series of photographs of the flame secured by means of a coupled stroboscope and piston, a device designed by Prof. G. S. Moler and kindly placed at my disposal for this purpose. Fig. 7 shows thirty successive phases covering one complete vibration of the flame.

When a narrow slit was placed before the flame so that the slit was perpendicular to the lower luminous edge, and the motion was examined by means of a revolving mirror having its axis parallel with the slit, it seemed probable that with proper adjustment of the slit a very good photographic record could be obtained. Accordingly a revolving film was arranged in a box so that an exposure could be made through a very narrow slit placed just in front of the film. The box was arranged so that it could be adjusted for focus and for position of the slit across the image of the flame. A shutter was connected with the wheel which carried the film in such a way that the exposure could be made at any time upon any quarter of the film.

Fig. 8 shows the result obtained from the telephone receiver with two different values of the alternating current. The boundary line which indicates the motion of the lower edge of the flame is very close to a sine curve. Curve (*a*) happened to be of such amplitude that it could be compared with Fig. 2 by superposition. The agreement was remarkably good, thus showing that both methods give the same wave form, and presumably the correct wave form of the source used.

Fig. 9 shows two curves from the telephone made to vibrate with another alternating current. The frequency of this current was 20, and it contained a very marked third harmonic. In (*b*) the phase of the harmonic was advanced 180° from what it was in (*a*).

Fig. 10 shows curves from the piston referred to above. In (*b*) the frequency was much greater than it was in (*a*). The peculiar form of these curves is due to the fact that the piston was vibrating in a cylinder closed at one end, and that the gas could leak around the piston. Record (*b*) is the curve which represents the vibration, the phases of which are shown in Fig. 7.

For the sake of comparison I have included photographs of two flame pictures. Fig. 11 (*a*) is the flame picture obtained when the telephone receiver is vibrated by the lighting current, and corresponds to the records shown in Fig. 2 and in Fig. 8. Fig. 11 (*b*) is the result when the piston vibrator is used, and corresponds to the record shown in Fig. 10 (*b*).

CONCLUSION.

It is doubtful whether the curves obtained from the vibrating flame by either of the above methods will serve as well as other means for analyzing sound waves. The curves shown by Professor D. C. Miller at the April, 1911, meeting of the Physical Society show far more promise for this purpose. As records from a vibrating flame, however, it is believed that they are of far more value than are any records heretofore obtained.

In all devices so far used in the analysis of sound waves, a correction must be made for the resonance effects, due to the free periods of the recording system, before the analysis is complete. In the case of the flame made to vibrate with the manometric capsule these effects are very small but certainly are not negligible. The preceding experiments show that a flame, made to vibrate by the variations in pressure of a sound wave within the gas jet, can be made to reproduce the curve which represents the form of the sound wave. If the flame could be made to vibrate with sufficient intensity by the variations in pressure of a sound wave in the free air outside of the gas jet, the resonance effects would be almost, if not wholly, eliminated. The observations of Marbe[1] and the results of some experiments which I have recently made seem to show that there is a possibility of accomplishing this result.

STANFORD UNIVERSITY,
August, 1911.

[1] Phys. Zeit., 8, 92, 1907.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FIFTY-EIGHTH MEETING.

THE regular fall meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, October 14, 1911, with President W. F. Magie in the chair.

The following papers were presented:

A Study of Simultaneous Tracings from the Apex of the Heart and the Radial Artery with the Micrograph. ALBERT C. CREHORE.

Torsional Rotatory Polarization. ARTHUR W. EWELL.

Spectral Luminosity Curves Determined by the Method of Critical Frequencies. HERBERT E. IVES.

A New Form of Gold Leaf Electroscope: A Null Instrument. J. C. HUBBARD.

The Electron Theory of Voltaic Force and Thermo-electricity. O. W. RICHARDSON.

The Influence of the Contact Difference of Potential between the Plates Emitting and Receiving Electrons liberated by Ultra Violet Light. K. T. COMPTON.

A Study of Tracings from the Region near the Apex of the Heart. ALBERT C. CREHORE.

A Study of the Presphygmic Period with the Micrograph. ALBERT C. CREHORE.

The Positive Ionization from Hot Salts. O. W. RICHARDSON.

On the Distribution and Direction of Motion of the Interference Bands of Light Formed by Thin Plates as the Thickness of the Plate Varies. ALBERT C. CREHORE.

A New Virial Theorem. D. F. COMSTOCK.

The Effect of Pressure on the Liquid and Five Solid Forms of Water. P. W. BRIDGMAN.

A Method of Determining Mean Reflection Coefficients. W. S. FRANKLIN and J. H. WILEY.

At the close of the program the meeting discussed briefly, in committee of the whole, the relations between the Society and the PHYSICAL REVIEW, Mr. Franklin acting as chairman. When the committee rose the chairman announced the adoption of the following resolutions:

1. *Resolved*, that this meeting requests the council to present to the society a plan by which the society shall publish a journal.

2. *Resolved*, further, that the council be requested to enter into negotiations with the editors of the PHYSICAL REVIEW to determine under what conditions the control of the REVIEW may be transferred to the society.

Adjourned at 1:30 P.M.

ERNEST MERITT,
Secretary.

THE ELECTRON THEORY OF CONTACT ELECTROMOTIVE FORCE AND OF THERMOELECTRICITY.[1]

BY O. W. RICHARDSON.

A DISCUSSION of the nature of contact electromotive force and of the laws of thermoelectricity on the view that metals contain a large number (n per c.c.) of free electrons, dynamically equivalent to the molecules of a gas, which are retained in the metal by the action of forces near the boundary giving rise to work functions, w_1, w_2, etc., characteristic of each metal. This hypothesis has already been very successful in accounting for the laws which regulate the emission of negative electrons from hot bodies. Extensive use is also made of the theorem which has been proved by writers on the kinetic theory with sufficient generality to cover the conditions postulated, that if W is the work done in taking an electron from a point A to a point B then

$$W = R\theta \log \frac{n_1}{n_2},$$

where R is the gas constant calculated for a single molecule, θ is the absolute temperature, and n_1 and n_2 are the concentrations of the free electrons at A and B respectively.

By considering the case of a number of electrons in a thermally and electrically insulated enclosure it is shown that the condition for equilibrium is the invariance of $w_A - eV_A - R\theta \log n_A$ for every point A in the enclosure: where e is the charge of an electron, V_A is the electric potential at A and w_A is the work done by an electron in escaping from the metal in which A is. If A is in the space between the conductors $w_A = 0$. It follows that there is a permanent difference of electric potential $V_m - V_0$ between any two conductors which is given by

$$V_m - V_0 = \frac{1}{\epsilon}\left\{w_m - w_0 + R\theta \log \frac{n_0}{n_m}\right\}$$

Experimental indications are that $w_m - w_0$ is much larger than the logarithmic term and is in all probability comparable with the observed Volta effects. If more complete knowledge of the values of the w's confirms these indications it would follow that the observed contact differences are intrinsic properties of the metals and not due to chemical action. Several weak points in the current evidence in favor of chemical action are pointed out.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

By considering the transportation of a number of electrons around suitable circuits of different metals and at different temperatures, so that the transference is partly along connecting conductors and partly through the surrounding space, but always in a resverible manner, it is shown that:

$$\pi e = R\theta \log \frac{P_2}{P_1} = R\theta \log \frac{n_2}{n_1},$$

$$\sigma = \frac{1}{\epsilon}\left\{\frac{Rr}{\gamma - 1} - R\theta \frac{d}{d\theta}\left(\log \frac{P}{P_o}\right)\right\} = \frac{1}{\epsilon}\left\{\frac{R}{\gamma - 1} - R\theta \frac{d}{d\theta}\left(\log \frac{n}{n_o}\right)\right\},$$

$$Te = R\int_{\theta_0}^{\theta'} \log\left(\frac{P_2}{P_1}\right) d\theta = \epsilon \int_{\theta_0}^{\theta'} \frac{\pi}{\theta}\, d\theta,$$

$$\frac{dT}{d\theta} = \frac{R}{\epsilon} \log \frac{P_2}{P_1} = \frac{\pi}{\theta} = \frac{R}{\epsilon} \log \frac{n_2}{n_1},$$

where π is the Peltier effect between the metals 1 and 2 at temperature θ, P_2 and P_1 are the respective pressures of the free electrons inside the same metals, n_2 and n_1 are the corresponding concentrations, σ is the specific heat of electricity, γ is the ratio of the specific heats of the electrons at constant pressure and constant volume. n_0 and P_0 are concentration and pressure of the internal free electrons at a fixed temperature θ_0, and n and P the corresponding quantities at the variable temperature θ. Finally T is the thermoelectromotive force of a circuit of the metals 1 and 2 whose junctions are at θ' and θ_0 respectively.

These formulæ agree with the results of Lord Kelvin's theory of thermoelectric phenomena, but they are not in entire accordance with formulæ which other writers on the electron theory have deduced by using other methods. Reasons are given, however, for believing them to be correct.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

THE INFLUENCE OF CONTACT DIFFERENCE OF POTENTIAL ON THE MEASUREMENT OF ELECTRON VELOCITIES IN THE PHOTO-ELECTRIC EFFECT.[1]

BY KARL T. COMPTON.

THE writer finds that when the velocities of the electrons liberated from metals by ultra-violet light are determined in the usual way, *i. e.*, by the relation

$$v = \sqrt{\frac{2P\epsilon}{m}},$$

where ϵ and m are the charge and mass associated with an electron and P is the greatest retarding difference of potential against which the electron can escape from the emitting plate, the results are incorrect unless the contact difference of potential between the emitting and receiving plates is added to the externally applied difference of potential.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

The following results are established.

I. When electron reflection is prevented by the use of a perforated screen and an auxiliary field, there is a shift of the "distribution of velocity" curves due, probably, to stray field through the perforations. This can be corrected for.

II. The contact difference of potential between the emitting and receiving plates must be added to the applied difference of potential when making measurements of the electron velocities.

III. When this contact difference of potential is corrected for, it is found that aluminium, zinc, brass, copper and platinum emit electrons with equal velocities.

IV. The shift of the "distribution of velocity" curves with the time since polishing the plates is accounted for by the time changes in the contact difference of potential between the plates.

The above results were obtained with plates tested in a high vacuum within a reasonably short time after polishing.

The writer expresses his indebtedness to Professor O. W. Richardson for his suggestions and advice during the investigation.

Palmer Physical Laboratory,
Princeton, N. J.

The Positive Ionization from Hot Salts.[1]

By O. W. Richardson.

THE paper describes experiments by the author which, together with those of Dr. C. J. Davisson,[2] show that the positive ions emitted by salts are metallic atoms which, in almost every case, carry a single electronic charge. The only indication of multiple charges is in the case of certain zinc salts where there is some evidence of the occurrence of positive ions with a charge equal to $2e$. The nature of the ions emitted by the salts is independent of the nature and pressure of the surrounding gas at low pressure, but it is necessary, in order to account for the values of e/m given by a number of salts such as aluminium phosphate, to suppose that the ions they emit do not come from the salt itself but from some impurity with which it is contaminated. Generally speaking the contaminations seem to be salts of the alkali metals, which are very efficient emitters.

The ionization produced by a large number of salts has been examined in gases (chiefly in air, however) at different pressures. The results are very complex and indicate that it is almost impossible to deduce anything as to the

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

[2] Phys. Rev., June, 1911.

nature of the ions from experiments of this character. A specimen of pure aluminium phosphate has been prepared which shows a very small ionization in comparison with either ordinarily pure aluminium phosphate or with the salts of the alkali and alkaline earth metals at the same temperature.

With some salts under certain conditions the decay of the positive ionization depends on the electrical field employed as well as on the time. A similar effect has already been shown by the author to characterize the positive ionization emitted by "new" platinum wires.

There is some indication that the action of vapors emitted by the salts on the hot platinum present in the apparatus is an important factor in the emission.

Torsional Rotatory Polarization.[1]

By Arthut W. Ewell.

EXPERIMENTS which have been reported upon previously,[2] demonstrated that torsional rotatory polarization is a joint effect of the twist and the accompanying transverse distortion. The latter produces double refraction and the former rotates the axes of this double refraction into an helical configuration. The theory of the phenomena has been worked out and the relation between the total difference of phase due to this double refraction (irrespective of the helical arrangement), the total angle of twist, and the rotation, may be expressed graphically. If a segment of a circle be constructed of aperture equal to twice the total twist, and whose arc is equal to the total difference of phase (in radians), the area of the segment is numerically twice the rotation (in radians).

It is difficult to measure the relative distortion of a twisted cylinder, and therefore cylinders were formed with an initial helical structure. The section was rectangular (to obtain simple strains), and when they were compressed at each point perpendicular to two of the opposite sides, they resembled optically and mechanically a twisted cylinder. For each such helical cylinder was prepared a similar straight cylinder which was compressed an equal amount. The difference of phase in the latter and the rotatory polarization of the former were observed. The observed rotations always agreed, within the limits of experimental error, with the rotation calculated by introducing the observed difference of phase and the angle of twist into the above graphical construction.

Worcester Polytechnic Institute,
Worcester, Mass.,
September, 1911.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

[2] Am. Jo. of Science, VIII., 1899, p. 89; XV., 1903, p. 363; Phys. Zeit. I., 1899, p. 201; V., 1903, p. 706; Johns Hopkins Univ. Cir., 1900, p. 64; Phys. Rev., XXXI., 1910, p. 607.

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Volume XXXIII. *December, 1911.* *Number 6*

THE

PHYSICAL REVIEW.

THE OPTICAL CONSTANTS OF ALLOYS AS A FUNCTION OF COMPOSITION.

J. T. Littleton, Jr.

Introduction.

MUCH work has been done in recent years in determining the optical constants of pure metals and in studying metallic dispersion, so that at the present time practically all the metals have been investigated with the exception of the more readily oxidizable ones. But while the metals have been carefully studied only scattering observations have been made on alloys and no study has been made of the effects of different percentages of the two metals alloyed. It is the purpose of this work to investigate different series of alloys, determining n (the refractive index) and k (the absorptive index) as functions of composition in order to associate any changes in the optical properties with changes in other physical properties of the metals.

Curves will be plotted between the optical constants and the percentages by volume of one metal. The percentage by volume rather than the percentage by weight is chosen partly on account of the fact that with this method of plotting some of the relations which would otherwise be more complex, become linear; partly, because this is the usual method applied to electrical conductivity curves for alloys and also because of the fact that in the theory of the optical properties of mixtures of dielectrics the volume proportion is used instead of weight proportion.

According to Drude's[1] theory the electrical conductivity is a function of N the number of electrons per c.c., and r the friction coefficient. He concludes that for short waves the optical properties depend upon N and not upon r, and that since N is unaltered by changes in the physica properties the optical constants should be affected to only a small extent by such changes. By alloying two metals, however, and forming a new compound or a solid solution of one metal in another, N can be changed and the study of the optical properties of these alloys should indicate such a change.

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[1] Phys. Zeits., I., 165, 1900.

The electrical conductivity of alloys changes in a way characteristic of the kind of alloy formed as the per cent. of the constituents is varied. In cases where the two metals do not mix but crystallize out separately, the conductivity of the alloys is related to those of the pure metals by a simple volume proportion as is illustrated by the curve in Fig. 1.

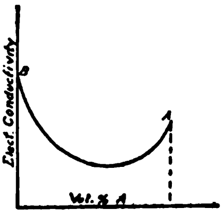

Fig. 1.

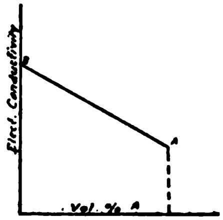

Fig. 2.

When the two metals are miscible in all proportions, forming in the solid state homogeneous mixed crystals, meaning by the term mixed crystal a crystal containing both metals, the conductivity has a minimum as is illustrated in Fig. 2.

If any part of the conductivity curve becomes a straight line the presence of two classes of crystals containing the metals in different proportions is indicated, while the curved portion means that for these percentages only one form of crystal exists. Compounds are indicated by sharp maxima or minima, while on melting point curves they are indicated by sharp maxima.

EXPERIMENTAL METHOD.

The apparatus used and the method followed in determining the optical constants is exactly similar to that of Drude and all others since who have used the Soliel modification of the Babinet compensator, consequently no experimental details need be given.

Since the absolute error in taking readings is nearly the same in all cases the percentage of error depends upon the magnitude of the angles measured and it will be stated after each table of results.

Sodium light was used in all cases, the necessary intensity being obtained with a blast lamp and sodium chloride in a platinum holder.

If ϕ be the angle of incidence of the light polarized in a plane inclined forty-five degrees to the plane of incidence, ψ the azimuth of restored polarization, Δ the relative change of phase occurring between the components of reflected light parallel and perpendicular to the plane of incidence, R the reflecting power, the subscript m referring to the means of observations at N different angles of incidence, then the optical constants are given in terms of these quantities by the ordinary Drude equations:

$$\sin\Delta \tan 2\psi = \tan Q,$$

$$\cos\Delta \sin 2\psi = \cos P,$$

$$\sin\varphi \tan\varphi \tan\frac{P}{2} = S,$$

$$n = \cos Q_m S_m \left(1 + \frac{\sum \sin^2\phi}{2S_m{}^2 N}\right),$$

$$k = \tan Q_m \left(1 - \frac{\sum \sin^2\phi}{S_m{}^2 N,}\right),$$

$$u = n(1 + k^2)^{\frac{1}{2}},$$

$$R = \frac{u^2 + 1 - 2n}{u^2 + 1 + 2n}.$$

$\bar{\phi}$ and $\bar{\psi}$ are the values of ϕ and ψ for which Δ has the value $\pi/2$. This position is called the position of principal incidence and the azimuth is called principal azimuth.

The question arises as to the meaning of the optical constants of alloys and the justification for applying these formulas for the computation of them. If alloys are made up of separate particles of the component metals, each one reflecting light just as does a finite surface of the metal, the resultant effect would be to produce an elliptical vibration capable of being analyzed by the Babinet compensator and giving data from which an n and a k might be computed. Optical constants so determined for such an alloy mean nothing. However if those alloys are studied which form mixed crystals of only one composition for each proportion of the component metals and also those alloys which are compounds, these may be considered as new metals and it will be perfectly justifiable to use this method of determining the optical constants.

It is quite difficult to obtain a polish which will give the true values of the optical constants and especially so with brittle alloys. Surface impurities of any kind tend to lower the value of Δ for a given angle of incidence, but fortunately Δ is not much affected by scratches. If a surface be scratched unidirectionally ψ changes when the surface is rotated in the plane of the scratches; different values of ψ are obtained according as the scratches are parallel or perpendicular to the plane of incidence. These facts allow a surface to be tested for what is called its normal state. If a metallic surface be freshly filed with a new clean file it must be in a relatively pure state and this gives values of Δ not far from correct. If subsequent observations made at different stages of polishing show a decrease from this value of Δ this indicates surface contamination and some other method of polishing has to be tried. The true value of ψ is obtained by taking the mean of ψ for the observations parallel and perpendicular to the scratches when the difference between them becomes a minimum. When this difference is zero and at the same time Δ has the largest value obtained the surface is said to give normal values of the optical constants. Such tests are easily and quickly made with the Babinet compensator. The details of polishing will be given later.

IRON-NICKEL ALLOYS.

Since iron and nickel form a doubtful compound at about thirty per cent. nickel by volume and since at this "compound point" there is a sudden change in many of the other physical properties of the alloys it is of interest to see whether any such change occurs in the optical constants. At this point the specific heat reaches a maximum five times that of pure nickel,[1] the thermal conductivity reaches a minimum one fifth that of pure nickel,[2] and the electrical conductivity also has a minimum of the same relative magnitude. Melting point observations do not prove the presence of the compound nor the complete miscibility of the two metals but the electrical conductivity curve given later will be taken as a proof of both of these points, the mixed crystals being composed of iron and the compound, and nickel and the compound.

These alloys were prepared by Professor James Aston, of the Electrochemical Department of the University of Wisconsin, and the physical properties just mentioned were determined from these specimens. Weighed proportions of electrolytic iron and nickel were melted in magnesia crucibles in an electric furnace of the resistor type, but in spite of all precautions some carbon was absorbed, as analysis proved, presumably from the carbon monoxide generated by the furnace, and for this reason these alloys may be called those of steel rather than of pure iron.

Before polishing, all the alloys were subjected to the same heat treat-

[1] Swartz and Muschel, B.A. Thesis, Univ. of Wis., 1910.

[2] Smith and Thomson, B.A. Thesis, Univ. of Wis., 1911.

ment which consisted in slowly cooling them from 950° C. in a platinum resistance furnace. The method of polishing which is used for steel and other hard metals worked equally well with these alloys. The specimens were mounted in a bed of wax and ground coplanar with wet carborundum of a coarse grade, known commerically as No. 70, on a rotating cast iron disk. Finer grades of carborundum were then used up to that which had remained in suspension in water for an hour, called sixty minute carborundum. Next the surfaces were ground with this last grade of carborundum on dry paper, though a wet canvas backing would have done just as well and would have been much more rapid. The polishing was done with twice-washed jeweller's rouge on an ordinary pitch tool, much of the success depending on getting this tool of the right consistency. Rosin and bees-wax were melted together using about the same amount of each and turpentine added until a drop cooled in water was fairly hard but no longer brittle. This was then poured on a checked metal disk, a thin layer of bees-wax added, and then figured. This tool was then covered with a generous supply of wet rouge and by a suitable mechanism moved over the surface to be polished, some pressure being applied. This method gave surfaces practically free from scratches and fairly plane, which after being brushed with dry rouge on chamois skin and washed with a fine grade of dehydrated alcohol gave the normal values for the optical constants.

If a softer polishing tool had been used the crystals would have polished into relief. This should not affect the value of the constants if the alloy were homogeneous but an image from such a surface does not give such good definition and observing is a little more difficult.

The means of the determinations are given in the following table.

The maximum deviation from the mean is 2 per cent. for n and 4 per

Iron-Nickel Alloys.

No.	Per Cent. Iron Vol.	$\bar{\phi}$	$2\bar{\psi}$	n	k	R Per Cent.
1	100	77° 8′	55° 38′	2.41	1.41	58.5
2	98.30	76° 49′	56° 2′	2.44	1.41	58.8
3	93.77	76° 47′	56° 00′	2.38	1.40	58.3
4	80.02	76° 45′	56° 58′	2.31	1.47	58.8
5	77.20	76° 40′	57° 00′	2.30	1.48	58.8
6	74.2	76° 37′	58° 10′	2.25	1.52	59.4
7	67.0	76° 25′	57° 21′	2.23	1.50	60.1
8	55.80	76° 44′	59° 50′	2.16	1.63	60.9
9	27.00	76° 30′	61° 37′	2.01	1.74	62.0
10	00	76° 1′	63° 22′	1.97	1.86	62.0

cent. for k. The values for pure nickel and steel are taken from Drude;[1] Nos. 2, 7, 6, and 8 were observed at angles of incidence equal to 68°, 70°, 72°, 74°, and 76°, and from the mean values of n and k $\bar{\phi}$ and $2\bar{\psi}$ were computed, while $\bar{\phi}$ and $2\bar{\psi}$ were measured directly in the cases of the remaining surfaces.

Curves are plotted between the optical constants and the per cent. of iron by volume. All points lie on the curves, within the limits of error. The resistance curve obtained from Professor Aston shows well where the compound is formed.

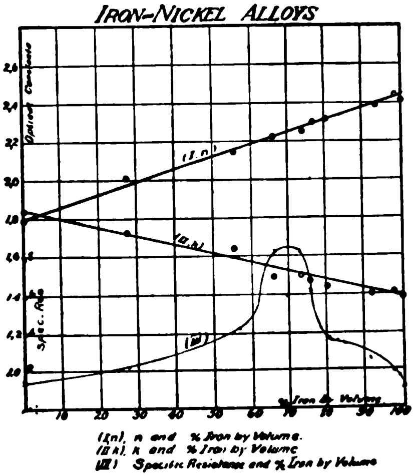

Fig. 3.

The optical constant curves show that n and k change linearly with the volume proportion, in contrast to the behavior of the other properties of the metals, and no compound is indicated.

Nickel-Silicon Alloys.

Since iron and nickel are in many respects so similar it was thought desirable to try the behavior of two metals having properties widely divergent. As a rule a complete series of such alloys which can be polished cannot be formed, but since nickel and silicon form an alloy of about eighteen per cent. silicon by weight and forty-seven per cent. silicon by volume which is supposed to be a strong compound and yet can be polished this series is of interest as far as it can be worked with. The physical properties of these alloys have not been studied to any extent.

Weighed proportions of pure nickel and pure silicon were melted together in an atmosphere of hydrogen, being heated up to 1600° C. in a graphite crucible in a carbon resistor furnace, at which temperature they were held for several hours and then quenched in water. Practically no oxidation had occurred, but on reweighing it was found that a small portion of the graphite had been dissolved, however it was less than one per cent., and since on cooling it solidified in separate crystals, it can have made no measurable difference in the results. Due to the extreme brittleness of these alloys they could not be polished when they contained more than twenty per cent. by weight of silicon. They were polished in the same way as the iron-nickel alloys but the process was more tedious and did not give such satisfactory results, due to the crystalline structure.

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[1] Ann. der Phy., XXXIX., 481, 1890.

Direct observations on $\bar{\phi}$ and $2\bar{\psi}$ give:

Nickel-Silicon Alloys.

No.	Per Cent. Si. Vol.	$\bar{\phi}$	$2\bar{\psi}$	n	k	R Per Cent.
1	0.	76° 1′	63° 22′	1.79	1.85	62.0
2	16.3	75° 53′	59° 8′	2.04	1.56	57.1
3	29.1	76° 5′	54° 30′	2.35	1.32	55.3
4	39.3	76° 14′	50° 15′	2.61	1.12	51.4
5	47.4	76° 24′	47° 50′	2.87	.99	50.6
6	100.	76° 45′	6° 52′	4.24	.114	37.7

There is a possible experimental error of 10 per cent. for n and k.

Curves are plotted between n and k and the per cent. of silicon by volume. These are straight lines well within the limits of error. There is no indication of the compound with forty-seven per cent. of silicon.

The melting point curve is given for comparison.[1]

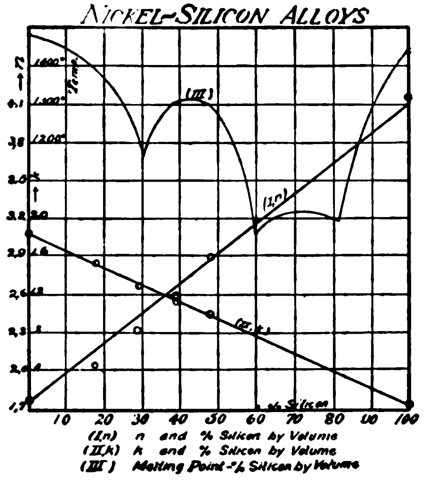

Fig. 4.

IRON-MANGANESE ALLOYS.

Manganese and iron form alloys containing an unbroken series homogeneous mixed crystals for all proportions which consequently are suitable for this optical test.[1] Barrett, Brown, and Hadfield[2] have shown that the electrical conductivity is decreased to about one fifth that of pure iron by an addition of fifteen per cent. of manganese and that for the same specimen, the thermal conductivity is decreased to about one half that of iron,[3] both changes being characteristic of this class of alloys.

Weighed proportions of iron and manganese were melted together in magnesia-lined graphite crucibles, being heated in a resistor furnace to about 1600° C. and left in the molten condition for about an hour in order to insure thorough mixing. Then the molten alloy was poured on a plane steel plate and allowed to cool. Annealing was necessary in order to get a uniform condition of crystallization.

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[1] Willian Guertler et G. Tamman, Zeit. an Chem., XLIX., 93, 1906.

[1] Levin et Tamman, Zeit. für an. Chem., 57, p. 136, 1905

[2] Barrett, Brown, and Hadfield, Inst. Elect. Eng. Jour., 31, p. 674, 1902.

[3] Barrett, Brown, and Hadfield, Roy. Dub. Trans., 102, Sept., 1904.

These alloys were polished in the same way as the nickel-copper alloys, giving very good surfaces practically free from scratches. Pure manganese could not easily be polished with rouge on account of the oxidation and consequently observations were taken on a surface scratched only in one direction with sixty-minute carborundum and the optical constants were computed from the mean of the observations parallel and perpendicular to the scratches.

Direct measurements of $\bar{\phi}$ and $\bar{\psi}$ give:

Iron-Manganese Alloys.

No.	Per Cent. Mn. Vol.	–	$2\bar{\psi}$	n	k	R Per Cent.
1	0	76° 30′	54° 58′	2.36	1.36	56.2
2	50	77° 43′	58° 3′	2.42	1.53	61
3	75	77° 55′	58° 30′	2.43	1.55	62.5
4	100	77° 54′	59° 10′	2.41	1.61	64.0

The above values are accurate to within three per cent. All points are on a straight line drawn through the end points of the optical constant curve well within this limit.

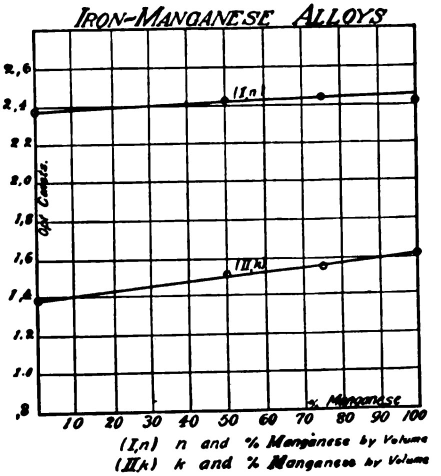

Fig. 5.

Wartenburg[1] gives for pure manganese $\bar{\phi} = 78° 13'$, $\bar{\psi} = 29° 15'$, $n = 2.49$, $k = 1.56$, $R = 63.5$ per cent.; and Freedericksz[2] $\bar{\phi} = 77° 34'$, $\bar{\psi} = 30° 10'$, $n = 2.25$, $k = 1.7$, $R = 63.5$ per cent.

ALUMINUM-COPPER ALLOYS.

Weighed proportions of aluminum and copper were melted together under a sodium chloride flux in ordinary clay crucibles. The melt was thoroughly stirred and cooled rapidly after being kept at a high temperature for two hours. Then the specimens were annealed for two hours longer at a temperature of seven hundred degrees. This method gives a mixture as nearly uniform as it is possible to get.

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[1] Ber. der Dut. Phy. Gesell., No. 3, 1910.

[2] Ann. der Phy., No. 4, p. 780, 1911.

Gwyer[1] by microscopical examination of etched surfaces of these alloys finds the following facts concerning their crystallography. The metals are thoroughly miscible from 100 per cent. copper to 75.5 per cent. copper by volume, forming in the solid state homogeneous mixed crystals of copper and aluminum. From 75.5 per cent. copper to 65 per cent. there are two forms of crystals of but at 63.5 per cent. there is again only one form of crystal present, agreeing with thermal data which indicate the formation of a compound at this point in the melting point curve. This compound is Cu_3Al. From this point to 30 per cent. copper there are homogeneous crystals of only one form present, but at 29 per cent. there are two kinds of crystals, accordingly the series of mixed crystals is said to end between 29 per cent. and 30 per cent. copper, and this point corresponds to the compound CuAl. The formation of this compound is not indicated on the melting point curve but there is an indication of it on the cooling curve. The alloys contain two forms of crystals from 29 per cent. to 25 per cent. copper where they have again only one form. This agrees with the thermal data which indicate the formation of the compound $CuAl_2$ at this point. From this point on to 1 per cent. copper there are two forms of crystals present.

Observations on these alloys were confined to those percentages having but one form of crystal, as indicated above, hence the application of the method is justifiable.

A slightly different method of polishing had to be used for these alloys. They were ground plane on carborundum cloth after being filed approximately true. Then they were ground with wet No. 150 carborundum powder on a cast iron disk covered with canvas. The disk was turned at a high speed for the more brittle alloys, giving a polish equivalent to that obtained with No. 00 emery paper. Finer grades were used up to rewashed sixty minute powder. The polishing was done with wet rouge on a cast-iron disk covered with "peau de soie" silk rotating at a slow speed, and continued until almost dry. The surfaces obtained by this method were free from scratches, fairly plane, and gave normal values for the optical constants, but there was a slight tendency for the crystal to polish into relief. To test the effect of this, one specimen was heated to redness, hammered out to about half its thickness and cooled in water. This showed no crystalline structure on polishing but the values of the optical constants were unaltered.

Measurements of $\bar{\phi}$ and $2\bar{\psi}$ directly give the following values:

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[1] Zeit. an. Chem., 57, p. 11, 1908.

Aluminum-Copper Alloys

No.	Per Cent. Al. Vol.	$\bar{\phi}$	$\bar{\psi}$	n	k	R Per Cent.
1	0	71° 35′	77° 54′	.641	4.08	83.5
2	19	73° 15′	76° 9′	.795	3.70	72.3
3	36.4	74° 34′	70° 7′	1.32	2.56	68.5
4	51.36	76° 16′	59° 56′	1.97	1.62	55.1
5	57.8	77° 5′	59° 25′	2.24	1.58	60.8
6	76	77° 30′	68° 4′	1.68	2.35	70.5
7	100	79° 55′	75° 8′	1.44	3.64	82.7

There is a possible error of two per cent. in n and three per cent. in k. The two end points are taken from Drude.[1]

The curves plotted between the optical constants and the per cent. of aluminum indicate the formation of the compound CuAl but there is not much evidence of the presence of the other two compounds, which are more clearly indicated by the thermal data, as previously mentioned. The only available electrical conductivity data on these alloys show a rapid decrease in the conductivity of copper for small additions of aluminum and there is a possibility that further study of the electrical conductivity would more conclusively prove the formation of CuAl than of either Cu_3Al or $CuAl_2$.

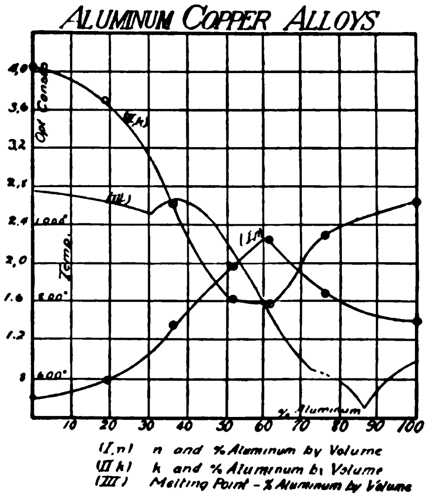

Fig. 6.

Copper-Nickel Alloys.

These alloys belong to a class containing only one form of homogeneous mixed crystals for all proportions, but forming no compounds, and having a characteristic electrical conductivity and melting point curve as already stated. They were formed by melting weighed proportions of the pure metals in graphite crucibles. After standing for four hours in the melted state in order that diffusion might be complete, they were cooled over night in the furnace, this giving a thoroughly homogeneous mixture.

In alloys containing high percentages of nickel some graphite was absorbed but as was shown by reweighing after melting the whole amount was less than one per cent.

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[1] Ann. der Phy., 39, p. 481, 1890.

Circular sections of about three centimeters in diameter were polished and gave good reflecting surfaces. The grinding was done by a method similar to that used for the copper-aluminum alloys, and the pitch tool process of polishing proved satisfactory.

Direct measurements of $\bar{\phi}$ and $2\bar{\psi}$ give the following results:

Copper-Nickel Alloys.

No.	Per Cent. Ni. Vol.	$\bar{\phi}$	$2\bar{\psi}$	n	k	R Per Cent.
1	00	71° 35′	77° 54′	.641	4.08	83.5
2	25	75° 58′	66° 12′	1.61	2.15	66.6
3	40	75° 41′	57° 46′	2.09	1.47	56.2
4	50	77° 8′	58° 32′	2.33	1.55	61.0
5	60	76° 15′	59° 0′	2.12	1.55	58.7
6	75	75° 30′	59° 0′	2.01	1.57	57.7
7	100	76° 1′	63° 22′	1.79	1.85	62.0

There is a possible experimental error in n of three per cent. and in k of four per cent.

Drude[1] gives the values of $n = 1.55$ and $k = 2.14$ for "coin metal" of approximately 75 per cent. copper and 25 per cent. nickel. This is in satisfactory agreement with the above values.

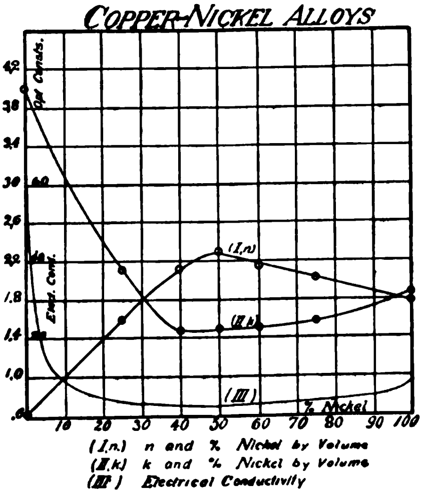

Fig. 7.

Bernouilli[2] gives the values of $n = .886$ and $k = 4.54$ for 3.94 per cent. Ni, and $n = 1.67$ and $k = 2.61$ for 17.3 per cent. Ni, which values do not agree with those here determined. However he uses an approximate formula; this, and a difference of polish could easily account for the discrepancy between our results.

The curve plotted between k and the per cent. of nickel by volume has very approximately the same general form as the conductivity curve determined by Feusner which is given for comparison. The curve between n and the percentage composition is the reverse. At least it can be said that the maximum n and the minimum k are found for the composition giving the minimum electrical conductivity.

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[1] Ann. der Phy., p. 523, 39, 1890.

[2] Verhand. der Phy. Gesellsch. zu Berlin, 109, 10, 1909.

IRON-COPPER ALLOYS.

Electrolytic iron and pure copper were melted in weighed proportions in a marquardt crucible, being held in the melted state for several hours and then cooled slowly. Stead[1] has shown that this method gives uniform proportions throughout the mixture.

There seems to be considerable difference of opinion among investigators as to the character of these alloys. Stead[1] claims that copper and iron are miscible in all proportions when free of carbon. Pfeiffer[2] maintains that the copper is only held in suspension in the iron, and Sahman[3] that there are two forms of crystals between three and eighty-nine per cent. copper by volume. If this latter statement be true the observations on this series cannot be said to determine much, for the reasons previously mentioned.

The same method of polishing which was applied to the aluminum-copper series was followed in this case.

Direct measurements of $\bar{\phi}$ and $2\bar{\psi}$ give the following values.

Iron-Copper Alloys.

No.	Per Cent. Iron Vol.	$\bar{\phi}$	$2\bar{\psi}$	n	k	R Per Cent.
1	0	71° 35′	77° 54′	.641	4.08	83.5
2	27.6	73° 50′	59° 15′	1.77	1.53	52.8
3	53.4	75° 36′	54° 57′	2.24	1.32	51.8
4	77.6	77° 17′	53° 40′	2.62	1.30	57.5
5	100	77° 07′	55° 38′	3.41	1.41	58.5

There is a possible experimental error of 2 per cent. in n and 3 per cent. in k.

The curves obtained by plotting n and k against the per cent. of iron by volume seems to be a straight line between 75 per cent. iron and 25 per cent. iron, but breaks very suddenly between these points and the ends. Conductivity data for any great range of composition are not available, but so far as known they show that small additions of iron to copper decrease the conductivity considerably.

DISCUSSION.

The above work brings out two points of interest. The first is the fact that for these six groups of alloys no increase in reflecting power over that of the pure metal is gained by alloying with a metal of a lower reflecting power. This is different from the results of Bernouilli[1] who obtains values for *n* and *k* for an alloy of 5 per cent. zinc and 95 per cent. copper which give a computed reflecting power of 91.2 per cent., while Drude gives the reflecting power of pure copper as 83.5 per cent. and of pure zinc as 78.6 per cent. The other point of interest is the fact that the optical constant curves are straight lines for the alloys of iron with nickel and with manganese, and the alloys of nickel with silicon; and on the other hand the optical constant curves depart very markedly from this linear form for the alloys of copper with iron, nickel, and aluminum.

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[1] Engineering, 851, LXXII., 1901.

[2] Metallurgie, 281, III., 1906.

[3] Zeits. an. Chem. G., LVII., 1908.

Before forming any hypothesis for an explanation of these forms of curves it will be well to review some of the other physical properties of these alloys and the metals forming them. The first thing to be noticed is that the "linear class" of alloys is formed of metals of a low electrical conductivity, while the "non-linear" class always has as one constituent a metal of relatively high electrical conductivity. This leads to the assumption that the linear relation is due to the low electrical conductivity of the two component metals. But some of the alloys of the coppernickel series have electrical conductivities much lower than either iron or nickel and just as low as any of the iron-nickel alloys. However this is further evidence in favor of the assumption, since the corresponding optical constant curves as here given are approximately straight lines beginning with the point of maximum resistance and ending with the metal of highest resistance.[2]

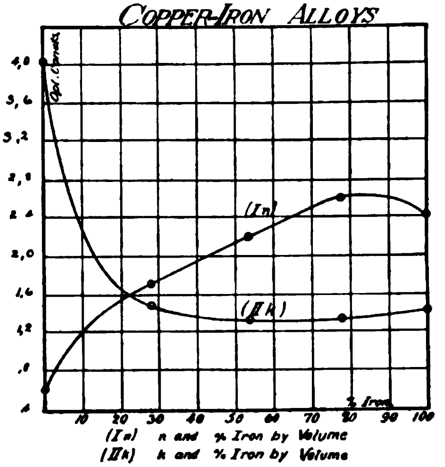

Fig. 8.

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[1] Bernouilli, Zeit für Elect. Chem., p. 15, 1909.

[2] Lorentz (Theory of Electrons, p. 147) has derived the expression

$$\frac{n^2 - 1}{n^2 + 2} = V_1\frac{(n_1^2 - 1)}{n_1^2 + 2} + V_2\frac{(n_2^2 - 1)}{n_2^2 + 2}$$

connecting the index of refraction of a mixture of dielectrics (n) with the indices of refraction of the components (n_1, n_2), and the volume percentages of the components present (V_1, V_2). It has been found that the indices of refraction of the *linear* class of alloys (iron-nickel, nickel-silicon, iron-manganese) satisfy the Lorentz equation for the most part within the error of observation. It is impossible without further data to decide which relation (the linear or the Lorentz) is the fundamentally important and which accidental. For alloys containing a low resistance metal, however, the Lorentz relation does not hold at all.

SUMMARY.

1. The alloys of iron with nickel, two metals with very similar properties, which contain a doubtful compound, have been studied. Although the alloys have quite different properties from those of the pure metasl the optical constants changed linearly with the change in the volume proportion of the two metals, and not as any of the other physical properties change.

2. The optical constants of nickel and silicon, two metals of quite different properties, the alloys of which form compounds, have been determined up to forty-seven per cent. silicon by volume. The linear relation between the optical constants and the proportion by volume is well illustrated.

3. Iron and manganese, two metals the alloys of which form mixed crystals, but no compounds, have been alloyed and the optical constants of the alloys determined. There is a linear change in the optical constants as the proportion of the metals is varied.

4. The optical constants of the alloys of copper and aluminum have been determined. This series contains three compounds and the formation of one is clearly indicated by optical data.

5. The optical constants of copper and nickel, two metals forming no compounds but being thoroughly miscible in all proportions, have been determined.

The optical constants do not change linearly, but follow very approximately the change in the electrical conductivity.

6. The optical constants of iron-copper alloys have been determined.

The curve plotted between the optical constants and the percentage composition has the general form of the characteristic conductivity curve belonging to this class of alloys.

7. It can be observed from the data on these alloys that there is no increase of reflecting power gained by alloying with a metal of lower reflecting power. The Lorentz law of refractivity deduced for dielectrics holds for high resistance metals but not for low.

Department of Physics,
University of Wisconsin,
June, 1911.

THE ACOUSTIC SHADOW OF A RIGID SPHERE, WITH CERTAIN APPLICATIONS IN ARCHITECTURAL ACOUSTICS AND AUDITION.

By G. W. Stewart.

THE discussion in this paper is limited to cases where the source of sound is located on a rigid sphere.

It is an extension of the work of Lord Rayleigh, and had as an incentive a query arising in architectural acoustics.

Theory.

The medium in which the vibrations occur is assumed to be uniform and to have perfect fluidity. If u, v, and w are the velocities of the particles in the directions of rectangular coördinates, and ρ the density, the equation of continuity is

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} + \frac{\partial (\rho w)}{\partial z} = 0.$$

Let $\rho = \rho_0(1 + s)$, where s is termed "condensation," and insert in the above equation. If we assume the wave length to be long in comparison with the amplitude of vibrations, we can neglect terms similar to $\rho_0 u \frac{\partial s}{\partial x}$ and $\rho_0 s \frac{\partial u}{\partial x}$ in comparison with $\rho_0 \frac{\partial s}{\partial t}$ and $\rho_0 \frac{\partial u}{\partial x}$.

We then have

$$\frac{\partial s}{\partial t} + \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0. \tag{1}$$

From this equation and the assumption that the forces are conservative, Lord Kelvin[1] showed that

$$\frac{D}{Dt}\int (udx + vdy + wdz) = 0.$$

This equation indicates that $(udx + vdy + wdz)$ is a perfect differential. Placing it equal to ψ, we have

$$\frac{\partial \psi}{\partial x} = u, \quad \frac{\partial \psi}{\partial y} = v, \quad \frac{\partial \psi}{\partial z} = w.$$

and ψ is the velocity potential.

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[1] Rayleigh, Theory of Sound, Vol. II., page 7.

We have from the general theory,[1] if the impressed forces are zero, a^2 representing $\frac{\partial p}{\partial \rho}$,

$$a^2 s = -\frac{\partial \psi}{\partial t}. \tag{2}$$

If the vibration is assumed simple harmonic, then the velocity and velocity potential are simple harmonic functions. Therefore,

$$\frac{\partial s}{\partial t} = k^2 \psi,$$

where $k = \frac{2\pi}{\text{wave-length}}$ and a is the velocity of sound.

Substituting these values in (1), we have our general equation for aerial vibrations,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + k^2 \psi = 0. \tag{3}$$

Expressing (3) in spherical coördinates, and multiplying by r^2, we have:

$$r^2 \frac{\partial^2 \psi}{\partial r^2} + 2r \frac{\partial \psi}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \omega^2} + k^2 r^2 \psi = 0. \tag{4}$$

The solution[2] of this equation is an infinite series, one term of which is

$$\psi_n = \frac{S_n}{r} e^{-ikr} f_n(ikr) + \frac{S_n'}{r} e^{+ikr} f_n(-ikr), \tag{5}$$

where S_n is a spherical surface harmonic of degree n, and

$$\begin{aligned} f_n(ikr) = 1 &+ \frac{n(n+1)}{2 \cdot ikr} + \frac{(n-1)\cdots(n+2)}{2 \cdot 4 \cdot (ikr)^2} \\ &+ \frac{(n-2)\cdots(n+3)}{2 \cdot 4 \cdot 6 \cdot (ikr)^3} + \cdots + \frac{1 \cdot 2 \cdot 3 \cdots 2n}{2 \cdot 4 \cdot 6 \cdot 2n (ikr)^n}. \end{aligned} \tag{6}$$

Inasmuch as ψ is assumed a simple harmonic function of the time, we may write

$$\begin{aligned} \psi_n &= \left[\frac{S_n}{r} e^{-ikr} f_n(ikr) + \frac{S_n'}{r} e^{+ikr} f_n(-ikr) \right] e^{ikat} \\ &= \frac{S_n}{r} e^{ik(at-r)} f_n(ikr) + \frac{S_n'}{r} e^{ik(at+r)} f_n(-ikr). \end{aligned} \tag{7}$$

The first term must represent a disturbance travelling outward, and the second a disturbance travelling inward. If we assume a rigid sphere, and locate the source upon it, the second term disappears, and we have

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[1] Rayleigh, Theory of Sound, Vol. II., p. 15.

[2] Ibid., p. 237.

$$\psi_n = \frac{S_n}{r} e^{ik(at-r)} f_n(ikr). \tag{8}$$

Assume that in the source the velocity is normal to the sphere, the radius of which is c. Let this velocity be represented by Ue^{ikat}, U being a function of the point considered. U can be expanded in a series of surface spherical harmonics,

$$U = U_0 + U_1 + U_2 + \cdots + U_n + \cdots.$$

When $r = c$,

$$\frac{\partial \psi_n}{\partial r} = U_n e^{ikat},$$

and from (8),

$$\psi_n = -\frac{c^2}{r} e^{ik(at-r+c)} U_n \frac{f_n(ikr)}{F_n(ikc)},$$

where

$$F_n(ikr) = (1 + ikr) f_n(ikr) - ikr f_n'(ikr), \tag{9}$$

and, finally,

$$\psi = -\frac{c^2}{r} e^{ik(at-r+c)} \sum \frac{U_n f_n(ikr)}{F_n(ikc)}. \tag{10}$$

The problem before us is to find the intensity of sound at any point, the sphere being rigid and hence neither absorbing nor transmitting the sound. In as much as our deductions are to be applied to architectural acoustics where the ear is the receiving instrument, we will consider intensity as referring to the potential energy, or energy due to s, the condensation. The reader should be reminded that in this problem, the kinetic energy of the progressive wave is not equal to the potential energy, since, in general, this would be true only of a plane progressive wave. The conditions of the problem preclude the possibility of a plane wave.

It can be easily shown that the energy per unit volume due to a condensation s is $\frac{1}{2}\rho_0 a^2 s^2$ where dp is equal to $\rho_0 s a^2$.[1] Referring now to (2), we have the energy per unit volume or the "intensity" proportional to

$$\left(\frac{\partial \psi}{\partial t}\right)^2.$$

If, now, we wish to compare intensities, we need merely to find the values of the relative intensities by means of the above expression.

Rayleigh[2] has utilized (10), assuming the source confined to a small area on the sphere in the neighborhood of $\theta = 0$, and obtains the following solution for the relative intensities at a great distance from the center of the sphere:

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[1] Rayleigh, ibid., p. 15.

[2] Rayleigh, ibid., page 254. For large values of kc, Rayleigh has put the solution in more convenient form. See Phil. Trans. of Roy. Soc., A, 203, p. 87.

Relative intensities are proportional to $F^2 + G^2$ where

$$F = \sum \frac{2n+1}{2} \frac{\alpha P_n(\mu)}{\alpha^2+\beta^2},$$

$$G = \sum \frac{2n+1}{2} \frac{\beta P_n(\mu)}{\alpha^2+\beta^2},$$

and

$$F(ikc) = \alpha + i\beta.$$

The values of α and β were obtained from (9) and (6).

We shall now consider the case where r is not great, and thus obtain a more general solution of the problem of the acoustic shadow. Equation (10) is simplified if we impose the conditions of our problem upon the general expression for U_n. U_n is the nth term of the surface spherical harmonic series,[1]

$$f(\mu, \omega) = \sum_{n=0}^{n=\infty} \left[A_{0,n} P_n(\mu) + \sum_{m=1}^{m=n} (A_{m,n} \cos m\omega + B_{mn} \sin m\omega) P_n{}^m(\mu) \right],$$

where

$$A_{0,n} = \frac{2n+1}{4\pi} \int_0^{2\pi} d\omega \int_{-1}^{+1} f(\mu, \omega) P_n(\mu) d\mu,$$

$$A_{m,n} = \frac{2n+1}{2\pi} \frac{(n-m)!}{(n+m)!} \int_0^{2\pi} d\omega \int_{-1}^{+1} f(\mu, \omega) \cos m\omega P_n{}^m(\mu) d\mu,$$

$$B_{m,n} = \frac{2n+1}{2\pi} \frac{(n-m)!}{(n+m)!} \int_0^{2\pi} d\omega \int_{-1}^{+1} f(\mu, \omega) \sin m\omega P_n{}^m(\mu) d\mu.$$

If we assume the velocity U to have the same value over the small area where $\mu = 1$, then,

$$f(\mu, \omega) = \sum_0^{n=\infty} \frac{2n+1}{2} P_n(\mu) \int U P_n(\mu) d\mu,$$

since the coefficients $A_{m,n}$ and $B_{m,n}$ become zero.

$P_n(\mu) = 1$, in the region where U is finite; $d\mu = \sin\theta d\theta$; element of area, $dS = 2\pi c^2 \sin\theta d\theta$; therefore,

$$U_n = \tfrac{1}{2}(2n+1) P_n(\mu) \int U d\mu = \frac{(2n+1)}{4\pi c^2} P_n(\mu) \int\int U dS.$$

Equation (10) therefore becomes

$$\psi = -\frac{e^{ik(at-r+c)}}{2\pi r} \int\int U dS \sum \frac{2n+1}{2} P_n(\mu) \frac{f_n(ikr)}{F_n(ikc)}. \qquad (11)$$

---

[1] Byerly's Fourier's Series and Spherical Harmonics, p. 204, using our symbols.

We shall now proceed to find the relative intensities at a distance r from the center of the sphere, remembering that the relative intensities are proportional to $\dot{\psi}^2$.

From (11),

$$\dot{\psi} = -\frac{ika}{2\pi r}e^{ik(at-r+c)}\int\!\!\int UdS\sum\frac{2n+1}{2}P_n(\mu)\frac{f_n(ikr)}{F_n(ikc)}.$$

Let

$$\dot{\psi} = -\frac{ika}{2\pi r}e^{ik(at-r+c)}(F+iG)\int\!\!\int UdS, \tag{12}$$

where

$$F+iG = \sum\frac{2n+1}{2}P_n(\mu)\frac{f_n(ikr)}{F_n(ikc)}. \tag{13}$$

Inasmuch as $\dot{\psi}$ is proportional to the condensation, we may take the real part of (12) which is

$$\dot{\psi} = \frac{ka}{2\pi r}(F\sin\gamma + G\cos\gamma)\int\!\!\int UdS, \tag{14}$$

where

$$\gamma = k(at - r + c).$$

In determining the intensities, we are concerned only with the average. Taking (14), squaring, and preserving only those terms which contribute to the average value, we have

$$\dot{\psi}^2 = (F^2+G^2)\left(\frac{ka}{2\pi r}\int\!\!\int UdS\right)^2.$$

Or, since relative values are desired, and intensity of source is assumed constant, we use the fact that $\dot{\psi}^2$ is proportional to $F^2 + G^2$.

It remains to determine the values of F and G.

Let

$$f_n(ikr) = \alpha' + i\beta', \tag{15}$$

$$F_n(ikc) = \alpha + i\beta. \tag{16}$$

Then according to (13),

$$F+iG = \sum\frac{2n+1}{2}P_n(\mu)\frac{\alpha'+i\beta'}{\alpha+i\beta}.$$

The following must then hold,

$$F = \sum\frac{2n+1}{2}P_n(\mu)\frac{\alpha\alpha'+\beta\beta'}{\alpha^2+\beta^2}, \tag{17}$$

$$G = \sum\frac{2n+1}{2}P_n(\mu)\frac{\alpha\beta'-\alpha'\beta}{\alpha^2+\beta^2}. \tag{18}$$

To solve a problem, then, the values of α, α', β, and β' in (15) and (16) are found by using (6) and (9); the substitution is made in (17) and (18); the relative intensities are then obtained by adding F^2 and G^2. The forms of the functions F and f, as far as $n = 6$ are given in the following:[1]

$$
\begin{aligned}
F_0(y) &= y + 1,\\
F_1(y) &= y + 2 + 2y^{-1},\\
F_2(y) &= y + 4 + 9y^{-1} + 9y^{-2},\\
F_3(y) &= y + 7 + 27y^{-1} + 60y^{-2} + 60y^{-3},\\
F_4(y) &= y + 11 + 65y^{-1} + 240y^{-2} + 525y^{-3} + 525y^{-4},\\
F_5(y) &= y + 16 + 135y^{-1} + 735y^{-2} + 2625y^{-3} + 5670y^{-4} + 5670y^{-5},\\
F_6(y) &= y + 22 + 252y^{-1} + 1890y^{-2} + 9765y^{-3} + 34020y^{-4}\\
&\qquad + 72765y^{-5} + 72765y^{-6},\\
f_0(y) &= 1,\\
f_1(y) &= 1 + y^{-1},\\
f_2(y) &= 1 + 3y^{-1} + 3y^{-2},\\
f_3(y) &= 1 + 6y^{-1} + 15y^{-2} + 15y^{-3},\\
f_4(y) &= 1 + 10y^{-1} + 45y^{-2} + 105y^{-3} + 105^{-4},\\
f_5(y) &= 1 + 15y^{-1} + 105y^{-2} + 420y^{-3} + 945y^{-4} + 945y^{-5},\\
f_6(y) &= 1 + 21y^{-1} + 210y^{-2} + 1260y^{-3} + 4725y^{-4} + 10395y^{-5}\\
&\qquad + 10395y^{-6}.
\end{aligned}
$$

The procedure is readily carried out if r and the wave length are somewhat larger than c. The desired accuracy can be obtained by taking a sufficient number of terms.

THE VARIATION OF SOUND INTENSITY WITH DIRECTION IN THE NEIGHBORHOOD OF A SPEAKER.

A question arises in architectural acoustics as to the effectiveness of reflecting surfaces in the neighborhood of a speaker, and the preceding theory furnished an opportunity for the computation of intensity in an ideal case which approximates the actual. It is assumed that the speaker is replaced by a rigid sphere, and that the source of sound is confined to the vibration in a small area of the sphere.

For computation, the sphere is assumed to be 60 cm. in circumference, and the wave length 120 cm., approximately that of middle C. The theory is now applied for a given value of r, the angle θ being made to vary. The accompanying Fig. 1 shows the geometrical relations. θ is zero directly in front of the speaker, and 180° directly in the rear of the speaker (the sphere).

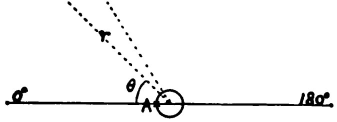

Fig. 1.

Computations have been made, using the values of c just given, several values of r and the following values of θ: 0°, 30°, 60°, 90°, 120°,

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[1] The forms of the function F are reproduced from Rayleigh's Theory of Sound, Vol. II., p. 238.

150° and 180°. The computations for the distance of 477 cm. ($kc = 0.5$ and $kr = 25$) follow. The values of α, α', β and β' were obtained by substituting the above values of r and c in (6) and (9), and are shown in Table I.

TABLE I.

n	α	β	α'	β'	$\frac{2n+1}{2} \times \frac{\alpha\alpha'+\beta\beta'}{\alpha^2+\beta^2} = A.$	$\frac{2n+1}{2} \times \frac{\alpha\beta'-\alpha'\beta}{\alpha^2+\beta^2} = B.$
0	+ 1.000	+ 0.500	+1.0000	0.0000	+0.4000	− .20000
1	+ 2.000	− 3.500	+1.0000	− .0400	+ .19753	+ .31569
2	− 32.00	− 17.500	+ .9952	− .1200	− .05589	+ .03995
3	− 233.00	+ 426.5	+ .9760	− .2390	− .004880	− .005340
4	+7,451	+4,070.5	+ .9282	− .3932	$+3{,}317\times10^{-7}$	$-4{,}187\times10^{-7}$
5	$+8{,}779\times10$	$-1{,}607.0\times10^{2}$	+ .8344	− .5732	$+2{,}706\times10^{-8}$	$+13{,}652\times10^{-9}$
6	$-4{,}120\times10^{3}$	$-2{,}250.0\times10^{3}$	+ .6759	− .7604	$-3{,}164\times10^{-10}$	$+13{,}728\times10^{-11}$

n	$P_n(\mu)$ $\theta=0°$.	$A\times P_n(\mu)$.	$B\times P_n(\mu)$.	$P_n(\mu)$ $\theta=180°$.	$A\times P_n(\mu)$.	$B\times P_n(\mu)$.
0	1.0000	+.40000	−.20000	+1.0000	+.40000	−.20000
1	1.0000	+.19753	+.31569	−1.0000	−.19753	−.31569
2	1.0000	−.05589	+.03995	+1.0000	−.05589	+.03995
3	1.0000	−.00488	−.00534	−1.0000	+.00488	+.00534
4	1.0000	+.00033	−.00042	+1.0000	+.00033	−.00042
5	1.0000	+.00002	+.00001	−1.0000	−.00002	−.00001
6	1.0000	.00000	.00000	+1.0000	.00000	.00000
		+.53711 $=F$	+.14989 $=G$		+.15179 $=F$	−.47083 $=G$
		$F^2+G^2=0.3108.$			$F^2+G^2=0.2446.$	

In finding the value of $P_n(\mu)$ for negative values of μ, the relations $P_{2n+1}(90° + \theta) = -P_{2n+1}(90° - \theta)$, and $P_{2n}(90° + \theta) = P_{2n}(90° - \theta)$

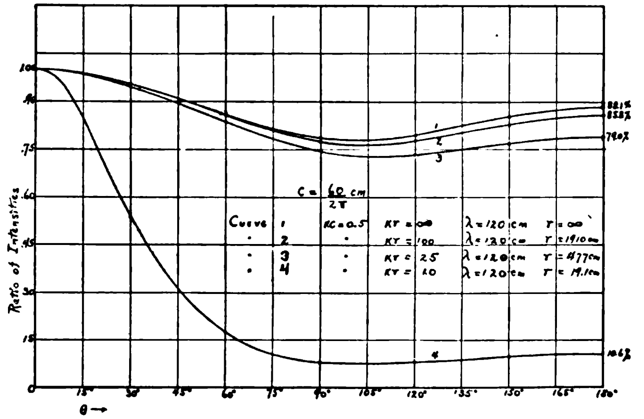

Fig 2.

were used. The values for $F^2 + G^2$ for the angles not given in the table were found to be 0.294 for 30°, 0.260 for 60°, 0.231 for 90°, 0.277 for 120°, and 0.237 for 150°. These values are plotted in Curve 1, Fig. 2, the one directly in front of the source, $\theta = 0°$, being given the value unity. The other curves exhibit the results for other distances. Of course the computed points are quite widely separated and the curves between them may not be correct. Computations for other angles would be needed if for any purpose greater accuracy is required. When $r = \infty$, the results agree with those obtained by Rayleigh, to which reference has already been made.

The results for two of the distances are again plotted in Fig. 3 for clearness. The curves in these figures show the presence of a minimum first mentioned by Lord Rayleigh, the variation with distance, indicating that the shadow is more marked the closer to the sphere (or to the speaker), and the importance of the reflecting surfaces in every direction in the neighborhood of a speaker.

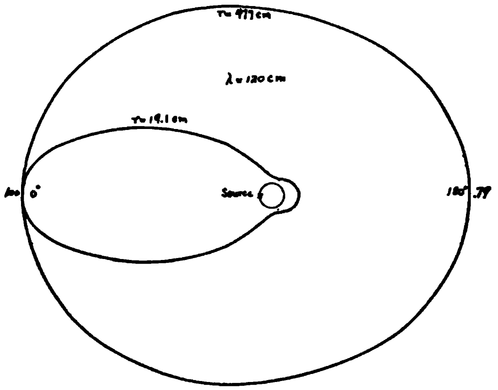

Fig. 3.

TABLE II.

Wave length, 240 cm., $kc = 0.25$, $kr = 12.5$.

n	α	β	α'	β'
0	+ 1.000	+ 0.2500	+1.000	0.000
1	+ 2.000	− 7.750	+1.000	− .08
2	− 140.0	− 35.75	+ .9808	− .24
3	− 953.	+3,732	+ .9040	− .4722
4	$+1,305\times10^2$	$+3,334\times10$	+ .7163	− .7463
5	$+1,439\times10^3$	$-5,638\times10^2$	+ .3667	− .9881

But we need to know what effect is produced by changing the wave length, the distance remaining constant. This effect I have ascertained

Wave length, 60 cm., kc = 1.0, kr = 50.

n	α	β	α'	β'
0	+ 1.000	+ 1.000	+1.000	0.000
1	+ 2.000	− 1.000	+1.000	− .0200
2	− 5.000	− 8.000	+ .9988	− .0600
3	− 53.00	+ 34.00	+ .9940	− .1198
4	+ 296.0	+ 461.0	+ .9820	− .1992
5	+4,951	−3,179	+ .9852	− .2966

Wave length, 30 cm., kc = 2.0, kr = 100.

n	α	β	α'	β'
0	+ 1.000	+ 2.000	+1.000	0.000
1	+ 2.000	+ 1.000	+1.000	− .010
2	+ 1.750	− 2.500	+ .9997	− .030
3	− 8.000	− 4.000	+ .9985	− .05998
4	− 16.19	+ 35.12	+ .9955	− .09998
5	+186.6	+ 85.44	+ .9895	− .1495
6	+538.8	−1,177.3	+ .9789	− .2087

by adopting wave lengths one octave lower, 240 cm., one octave higher, 60 cm., and two octaves higher, 30 cm. The distance, r, remains 477 cm. The following table gives the values of α, α', β, and β' for these three additional wave lengths.

The results of computation[1] with the above values are exhibited in the curves of Fig. 4,[2] together with the values already given for the same distance and 120 cm. wave length.

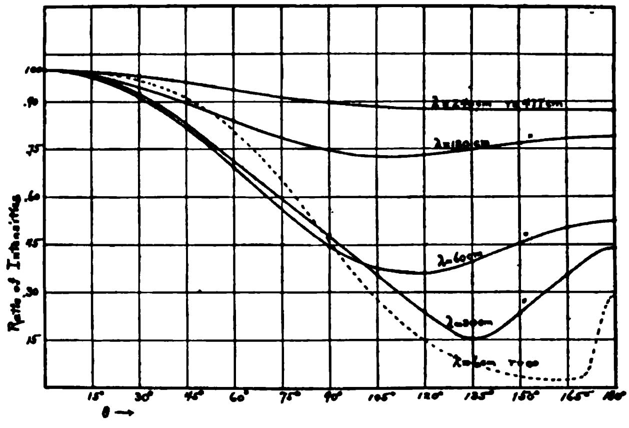

Fig. 4.

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[1] The computations involved in Figs. 2 and 3 have been very carefully checked and are correct to four significant figures. Those exhibited in Fig. 4 have not been so carefully checked, but are thought to be correct to three significant figures.

[2] The dotted curve represents Rayleigh's results for $KC = 10$, which are referred to elsewhere.

It is here to be observed that a change in pitch makes a marked difference in the shadow. With the wave length 240 cm. there is no minimum discernible. The variation between the 240 cm. and 120 cm. curves is much less than between the 120 cm. and 60 cm. curves. This shows that the shadows at first change slowly with diminishing wave lengths or sounds of higher pitch. Clearness of enunciation depends largely upon tones considerably higher than the fundamental. It is evident, then, that no curve can be drawn which truly represents the shadow, for the effective shadow (judging by clearness) would be different for different vowels, for different consonants, and hence for different words. We are compelled to leave the matter in this indefinite state, utilizing the curves already exhibited as a general guide. These curves probably limit all others representing the shadows which would occur with the tones in the selected three octaves, so that they give a fair picture of what occurs for that particular range.

Our conclusions are: (1) that an exact statement of the importance of reflecting surfaces in various locations cannot be given, even admitting the approximation involved in the substitution of the sphere for the speaker, for clearness of speech depends upon very complex tones; (2) that the intensity in the rear is generally (not for a wave length of 30 cm.) greater than at any point in the rear hemisphere surrounding the speaker; (3) that the results exhibited in the accompanying curves are sufficiently definite to indicate that the reflecting surfaces at any point in the neighborhood of a speaker are too important to neglect. It is to be noted that the effectiveness of reflecting surfaces is not here being discussed save in so far as that effectiveness is determined by the intensity of sound.

APPARENT INTENSITY OF SOUND FROM A SOURCE AT A DISTANCE AS DEPENDENT UPON THE POSITION OF THE HEAD.

The above topic is of considerable interest because of its bearing upon the perception of sound direction. Rayleigh[1] has discussed the effect of the position of the head upon the ratio of the sound intensities at the two ears, with the source at a distance great in comparison with the wave length of sound. The theory developed in this paper makes possible its application in case the source of sound is not at a great distance. The application is made possible by Hemholtz's reciprocal theorem. This may be stated as follows:[2]

"If in a space filled with air which is partly bounded by finitely extended fixed bodies and is partly unbounded, sound waves be excited at any pont A, the resulting velocity potential at a second point B is the same both in magnitude and phase as it would have been at A had B been the source of sound."

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[1] Rayleigh, Phil. Mag., XIII., 1907, p. 214.

[2] Rayleigh, Theory of Sound, Vol. II., p. 294.

The preceding theory found the relative intensities with varying angle θ at a given distance from the center of the sphere with the source at A (see Fig. 1). Thus the relative intensities at points A', A'', etc., were obtained. The reciprocal theorem states that the velocity potential at A, when the same source is removed to A', is equal to the velocity potential which was formerly at A'. Thus with the source at A', the velocity potential at any and at all points of the sphere can be ascertained.

Inasmuch as the reciprocal theorem states that the veloctiy potential is the same in phase as well as magnitude, then the values of $\dot{\psi}$ and $\dot{\psi}^2$ can be considered the same. We can thus use the reciprocal theorem to refer to intensities (due to pressure) as well as to velocity potentials.

The values for intensities will be taken from the curves already exhibited, the assumption being made that the head approximates a rigid sphere, with the ears diametrically opposite. In obtaining the sum[1] of the relative intensities at the ears due to a source of sound at a distance r, we will need to add the values for θ and $(180° + \theta)$. Since the intensity at $(180° + \theta)$ is the same as at $(180° - \theta)$, we will obtain the sum by adding θ and the latter.

The effect of distance upon the apparent intensities will first be considered. In the accompanying Fig. 5 are exhibited the results obtained

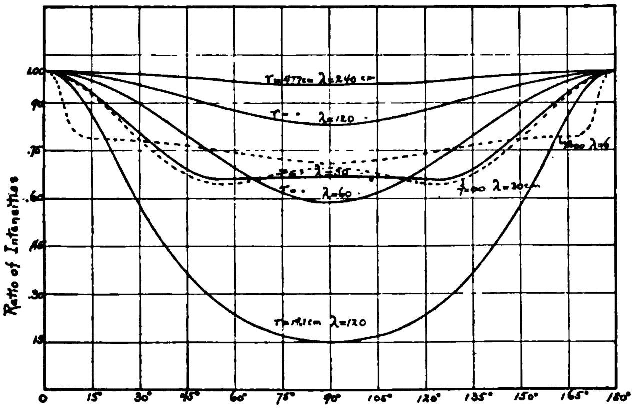

Fig. 5.

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[1] The sum of the relative intensities is plotted in preference to the ratio of intensities. Reasons for this will be made clear in a subsequent paper. We here assume that the apparent intensity is the sum of the two intensities, and the relative values of the sum are plotted in Fig. 5. It should be noted that no attention is paid to phase differences.

when the source is at 477 cm., and at 19.1 cm. The curves describe the effect with 180° rotation of the head, although 90° would have been sufficient. The resulting apparent intensity is the greatest when the diameter connecting the ears is in the direction of the sound source. Also, the variation of the apparent intensity with the position of the head is more marked the nearer the source to the hearer, the maximum intensity being sharper and the maximum variation greater.

In Fig. 5 are also exhibited the relative apparent intensities for the wave lengths 240 cm., 60 cm., and 30 cm. Here are also represented by the dotted lines the results of Rayleigh[1] for $kc = 2$ (wave length 30 cm.), and $kc = 10$ (wave length 6 cm.), r being considered infinite in both cases. It is evident that in each case the position of the maximum apparent intensity is that of 0°–180°, or the ear toward the source. Furthermore, the maximum apparent intensity is more sharply marked as the pitch of the sound becomes higher.

The fact that the position of the minimum does not remain at 90° with decreasing wave length is somewhat surprising. A reference to Fig. 4 and a recognition of the movement of the minimum intensity toward 180°, shows why the apparent intensity in the 90° position should not continue to be a minimum with increasing frequency.

As pointed out by Rayleigh, one of the factors of importance in the location of the source of sound is the variation of apparent intensity with the position of the head. The evidence from these curves would be that for low tones, the intensity factor is not very effective, for the apparent intensity is almost the same in any position. With tones somewhat higher, this factor would seem to become more effective. But with tones still higher, wave length 30 cm. and less, its importance again diminishes. The dotted lines can be considered as an approximate representation of what occurs at the wave lengths stated and a distance of 477 cm.

The foregoing results are obviously only approximate, for we have assumed the head to be equivalent to a rigid sphere with the ears diametrically opposite. With this limitation we can conclude: (1) that the apparent intensity is always greatest when the head is turned with an ear toward the source, the 0°–180° position; (2) that the variation of the apparent intensity with the position of the head is more marked the nearer the source to the hearer; (3) that with decreasing wave length the maximum value of apparent intensity occurs with greater sharpness; (4) that the maximum variation of apparent intensity is least with lowest tones; (5) that the maximum variation of apparent intensity does not increase without limit, for at wave length 30 cm. it has already commenced to decrease.

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[1] Rayleigh, Phil. Trans. Roy. Soc., A, 203, p. 87.

SUMMARY.

This paper discusses the acoustic shadow of a rigid sphere in terms of intensities due to pressures, when the source is located on the sphere and when the distances at which the intensities are determined are not large in comparison with the sphere. The analysis of the problem is presented and two applications of the solution are presented: (1) the effectiveness of reflecting surfaces when placed in various positions in the neighborhood of a speaker, the effectiveness being judged by the intensities only; (2) the apparent intensities of sound from a source at a distance as dependent upon the position of the head, which is of interest because of its bearing upon the perception of the direction of sound. The conclusions are presented with sufficient brevity under the topics discussed.

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ARTIFICIAL ROTATORY POLARIZATION.

By Arthur W. Ewell.

Introduction.

IN 1899 the writer discovered that a twisted jelly cylinder shows rotatory polarization, the plane of polarization being rotated in the opposite direction to the twist. During the next four years the following quantitative relations were established and published.[1] The rotation is independent of the distance of the path of the light from the axis of the twisted cylinder, but decreases with increasing obliquity between these two directions; is increased by inclosing the jelly cylinder within a tightly fitting rubber tube; is independent of hydrostatic pressure; decreases with rise of temperature; and usually exhibits mechanical, and resulting optical, relaxation effects. The rotation of rubber-covered jelly cylinders was proportional to a high power of the twist, the mean value of this power being approximately four, and the rotation increased with longitudinal compression.

This investigation was resumed two years ago with improved apparatus and materials.

Apparatus.

All observations of the rotation were made with a Schmidt & Haensch half shade polarimeter. Sodium light was usually used. When a more intense light was required, a Nernst lamp was employed with abiquartz cut for sodium light. In studying the dispersion, three approximately monochromatic lights were obtained by filtering the light from an electric arc through glass cells filled with Landolt's solutions.[2]

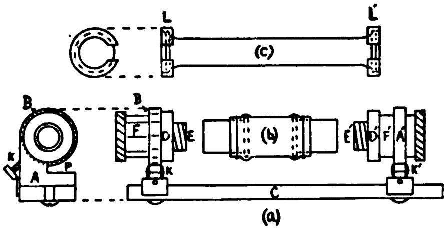

Fig. 1.

Fig. 1 (*a*) represents the final form of apparatus for applying and measuring twists. The clamps, *A*, can be fastened at different points on the bar, *C*. The upper portion of each is curved, and slotted at *P*, so as to fit the tray of the polarimeter, and permit rotation (change of azimuth) of 135° without displacement of the axis. Each clamp is carefully bored to receive a tube, *F*, the axis of which coincides with the axis of the polarimeter when the clamps rest in the tray. The edge of the hole was graduated into 10° intervals (*B*), and each tube, *F*, was ruled longitudinally with eight lines 45° apart. Rubber-covered cylinders (Fig. 1, *b*) were held by nipples, *E*, which screwed into both the tubes of the jelly cylinders and the collars, *D*. The glass plates of bare cylinders (Fig. 1, *c*) and the fiber disks of glass rods, were held by slotted collars, *L*, which replaced the collars, *D*. *F'* was clamped by the screw *k'* and the cylinder was twisted by rotating *F*, the angle being read on *B*, any convenient one of the lines on *F* being used as an index. The azimuth in the polarimeter tray was read by a scale on the outside of *A*.

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[1] Am. Jo. of Science, VIII., 1899, p. 89; XV., 1903, p. 363; Phys. Zeit., I., 1899, p. 201; V., 1903, p. 706; Johns Hopkins Univ. Cir., 1900, p. 64.

[2] Mann, Manual of Advanced Optics, p. 185.

In accordance with the customary notation of polarimetry, dextrorotation will be called positive, *i. e.*, a positive rotation or twist is one which appears clockwise to the observer of either the light or the twisted cylinder. The position of the analyzer was always observed for at least four different azimuths of the torsion apparatus just described, successive azimuths differing by 45°. The rotation was deduced from the average of the four readings. The jelly itself is "active," and the natural rotation was always observed for each color, and subtracted.

MATERIALS.

Glass.—Two circular glass rods, over 20 cm. long and 4.9 mm. in diameter were obtained from Carl Zeiss, of Jena. The ends were very plane and no strain was discernible in polarized light. Fiber disks were slipped over the ends and attached with "cementium." One of these rods was later ground to an elliptical cross section, the two diameters being 4.86 mm. and 4.18 mm.

Jelly.—The mechanical and optical properties of jelly preëminently adapt it for such investigations. The most satisfactory jelly consisted of gelatine, water and glycerine in the proportion of one gram of gelatine[1] to 4 cm^3 of water plus 3 cm^3 of glycerine. Air bubbles are excluded with difficulty if more gelatine is used, and, if the jelly is made thinner, relaxation effects become troublesome. A weighed mass of gelatine was allowed to absorb nearly the required amount of cold water. Surplus water was removed, and the pulpy mass was weighed The deficient water was then added, together with the glycerine. The whole was gradually heated and stirred until all the gelatine dissolved. The liquid was then filtered, both filter and beaker for filtrate being surrounded by steam jackets. Careful stirring immediately before pouring into the mould prevented inhomogeneity.

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[1] Gelatine No. 201, of Paul Koepff, Goeppingen, Würtenberg.

The rubber covered jelly cylinders were constructed as follows. A circular glass plate which had been cemented to one end of a slightly smaller threaded brass tube, was inserted into each end of a slightly smaller tube of pure gum rubber (Fig. 1, *b*). Wire bands secured the rubber and brass tubes. Melted jelly was poured into the tube through a slit in the side, air bubbles being carefully excluded, and the jelly was allowed to solidify while the tubes were held in alignment.

Bare and metal-covered cylinders required more elaborate preparation. A thin layer of jelly will adhere strongly to glass if it solidifies under exposure to the air, and masses of jelly will adhere if they are partially liquid when brought into contact. A large body of jelly only adheres to glass by suction, and they separate under strain unless there is an assisting envelope. The following method of attachment was however successful. Two suitable glass plates were covered with a thin layer of the jelly. When this had set, they were again dipped in the melted jelly and immediately clamped in a frame, one parallel to and directly above the other. A metal or paper tube was immediately placed upon the lower plate, and melted jelly was poured into the tube until about to overflow, when the upper glass plate was lowered upon it. Stops held the tube in correct alignment with the glass plate. Both interior and exterior of the tube were lubricated with vaseline, and when the jelly solidified, it did not adhere to the tube, but did adhere strongly to the glass plates. If a bare tube was desired, a paraffined paper tube was used, which was cut away after the jelly had solidified.

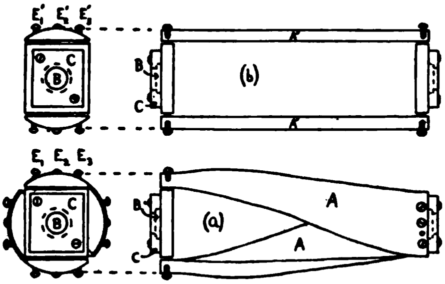

Fig. 2.

In the final experiments, the jelly was cast between the plates, *A*, *A*, or *A'*, *A'*, of Fig. 2 (*a*) and (*b*). The inside of these plates was plane. The moulds were closed by vaselined strips of lead, which were held against the plates by wire bands. The whole was then placed in a slightly larger, vaselined, brass tube closed at one end. One of the glass cover plates, *B*, was removed for pouring in the jelly. When the jelly had solidified, the brass tube was slipped off, and the lead strips removed, leaving either an helical or straight cylinder of rectangular cross section.

Experimental Results.

To economize space, most of the results are presented graphically, without tables. Curves I. (Fig. 3) were obtained with a jelly cylinder 3.9 cm. long and 1.8 cm. in diameter with a rubber envelope 0.28 cm. thick. For Curves II. the respective dimensions were 3.7 cm., 1.15 cm., and 0.235 cm., and for Curves III., 4 cm., 0.6 cm. and 0.175 cm. The subscript "*a*" signifies that the light employed was of approximate wave-length 6,560 Å.U., "*b*" wave-length 5,330, and "*c*" wave-length 4,480. The rotations which are plotted are the averages of the artificial rotations, for the two directions of twist, after reduction to a common length of 4 cm. (see below).

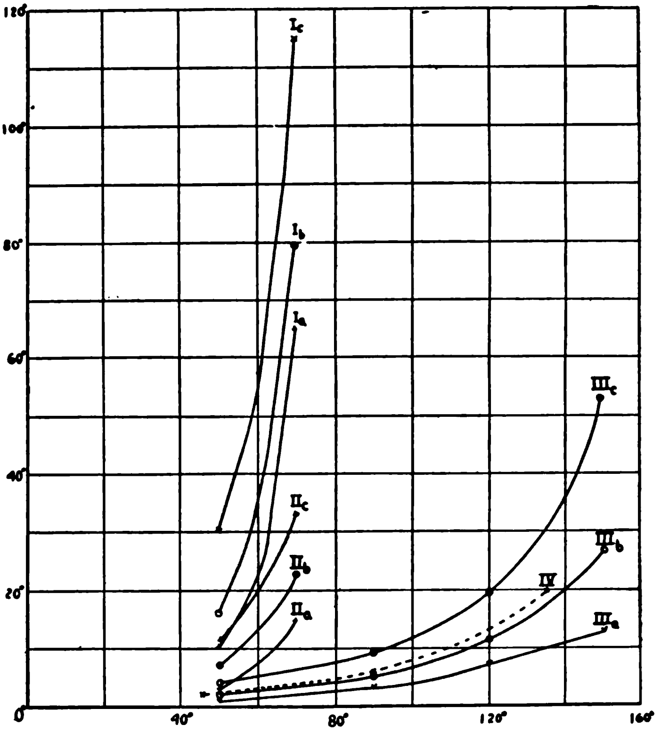

Fig. 3.

Abscissas = twist (degrees). Ordinates = rotation (degrees).

A comparison of the three sets of curves shows that *the artificial rotation is approximately proportional to the square of the diameter.*

The abscissas of Fig. 4 are the logarithms of the wave-lengths of the light employed and the ordinates are the logarithms of the rotation. The inclination of the lines demonstrates that *the artificial rotation* *(represented by the full lines) is approximately inversely proportional to the square of the wave length.* Since there was some uncertainty about the exact wave-length, it is important to observe the close parallelism between these lines and the dotted lines which give the logarithms of the natural rotation.

To illustrate the individual observations, the readings for Fig. 3, Curves I., *a*, *b*, and *c*, 70° twist, are given in full in Table I. The zero of the instrument was 5.30°, and the mean positions of the analyzer before the jelly was twisted, for the three wave-lengths were 359.7°, 355.9° and 348.2° respectively.

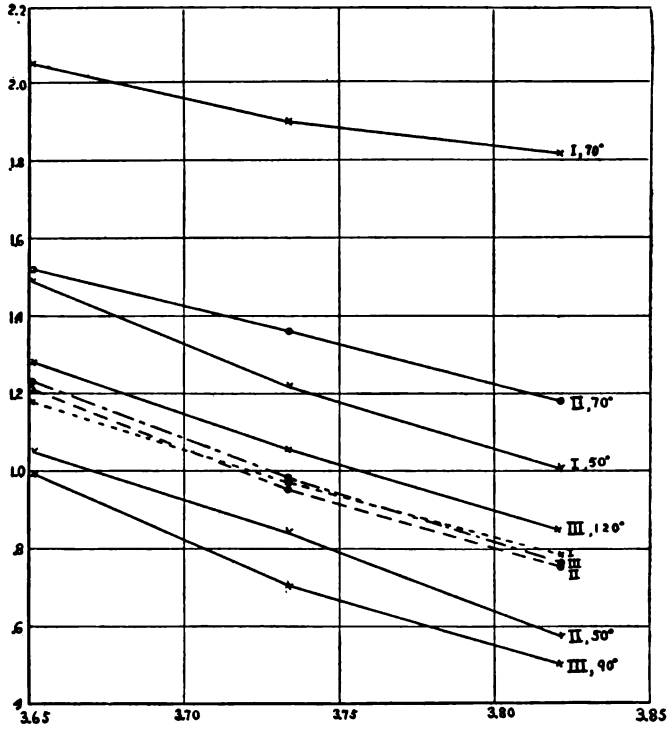

Fig. 4.

Abscissas = logarithms of wave-length of light in Angström units. Ordinates = logarithms of rotation in degrees.

Curve IV. represents observations similar to those of II., *b* except that the length of the cylinder was 7.7 cm. This and similar comparisons demonstrated that *the artificial rotation is approximately inversely proportional to the square of the length.*

We will now consider certain experiments which suggest the function of the envelope, for as stated in previous papers, the rotation of a jelly cylinder is greatly increased by a rubber envelope.

TABLE I.

Twist.	Position of Analyzer.		
	6,560 Å.U.	5,330 Å.U.	4,480 Å.U.
+70°	296.4	290.2	226.7
	301.2	279.8	268.3
	302.2	290.0	212.2
	295.3	270.6	234.2
Mean	298.8	282.6	235.4
Artificial rotation	− 60.9	− 73.3	−112.8
−70°	79	91	85
	77	89	111
	68	91	150
	77	91	117
Mean	75.2	90.5	115.8
Artificial rotation	+75.5	+94.6	+127.6
Mean artificial rotation	67.2	83.9	120.2
Reduced to 4 cm. length	64.0	79.8	116.0

In cylinder I. of Table II. the jelly adhered to the rubber envelope, while with cylinder II. adherence was prevented by a film of vaseline. If allowance in made for a slight difference of length, the rotations are practically identical.

TABLE II.

Mean Artificial Rotation for 90° Twist.

	6,560 Å.U.	5,330 Å U.	4,480 Å.U.
Cylinder I.	11.7	18.4	29.8
" II.	9.1	15.6	24.7
" III.	1.6	2.8	3.9

It was early noticed that an apparently circular rubber tube became elliptical when twisted and that the ellipticity increased with the twist. If the jelly cylinder is constrained to preserve its original cross-section, the rotation is very small. Cylinder III. of Table II. was similar to cylinder I. except that a brass tube, vaselined inside, enveloped 2.55 cm. of its length of 3.3 cm. If the rubber tube of a cylinder such as II. was cut next the glass end plates, the jelly alone twisted, the rubber tube was not distorted, the approximate circular cross-section of the jelly was preserved, and the artificial rotation became practically zero.

Jelly cylinders cast inside circular metal tubes gave only very small artificial rotations. Contrary to the results with rubber envelopes, stretching somewhat increased the rotation. By separating the jelly from the tube, the stretching permitted the cylinder to assume an elliptical form. These examples prove that *distortion of the cross-sections is a necessary condition for artificial rotation.*

As one would therefore naturally expect, a cylinder with an initial elliptical cross-section shows a greater rotation than one with an apparently circular cross-section, as the following typical examples illustrate. Cylinder I. of Table III. was a rubber-covered, elliptical cylinder 3.7 cm. long and the diameters of the cross-section were 1.4 cm. and 1.1 cm. II. was a similar, circular, rubber-covered cylinder 1.15 cm. in diameter. III. was a *bare* elliptical cylinder 3.9 cm. long and the diameters of the cross-section were 1.85 and 1.35 cm. IV. was a similar *bare* circular cylinder 1.6 cm. in diameter.

Table III.

	Twist.	Mean Artificial Rotation.		
		6,560 Å.U.	5,330 Å.U.	4,480 Å.U.
Cylinder I.	50°	10.6	16.3	30.6
" II.	50°	4.4	8.1	13.2
" III.	135°	12.5	27.0	47.0
" IV.	135°	3.7	7.6	13.7

Since the shape of the rubber envelope was so important a factor the author investigated the *influence of twist upon the distortion of rubber tubes filled with jelly*, and obtained the following results: *The sum of the proportional changes in the two diameters of the elliptical cross-section is approximately proportional to the diameter, increases with longitudinal compression, and is proportional to a higher power of the twist than the first.*

THEORY.

The preceding experiments indicate that the artificial rotation is due to the distortion of the cross-sections, and their helical orientation. The increasing ellipticity of the cross-sections as the twist is increased, must produce double refraction, the axes of the strain being the major and minor diameters of the ellipse. The continuous orientation of these axes in the twisted cylinder suggests Reusch's[1] packets of helically arranged, double refracting plates. The theory of the latter has been worked out by Poincaré,[2] Sohncke,[3] and Mallard,[4] and is excellently presented by Mascart.[5]

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[1] Pogg. Ann., CXXXVIII. (1869), p. 628.

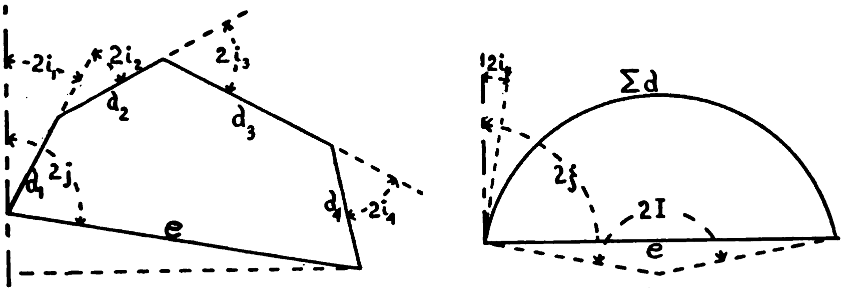
[2] Lumière, II., p. 276.

[3] Pogg. Ann. Erganzungsband, VIII. (1878), p. 16.

[4] Ann. des Mines, X. (1876), p. 60; XIX. (1881), p. 256.

[5] Traité D'Optique, II., p. 323.

Let the differences of phase, in angular measure, produced by the different plates be d_1, d_2. . . . Let the angle between the initial plane of polarization and the principal section of the first plate be represented by i_1, between the principal section of this plate and that of the second plate by i_2, etc. Starting from a vertical axis (Fig. 5, *a*), lay off a line numerically equal to d_1 at an angle $2i_1$. At its extremity add a line numerically equal to d_2 at an angle $2i_2$ with d_1 produced, and so continue, finally closing the polygon with a line of length e at an angle $2j$ with the initial axis. Mascart shows that if S is the area of this polygon and U is the angle of rotation in radians



(a) (b)

Fig. 5.

$$U = \frac{S}{2} - \frac{e^2 \sin 4j}{8}$$

and that the direction of the rotation is opposite to the helical structure.[1] The rotations calculated in this manner agree well with the experimental results. We will now extend this theory to twisted cylinders, and show that it explains all the observations.

A twisted cylinder with a distorted cross-section may be considered as composed of similar, infinitely thin, double refracting plates, the principal section of each plate being rotated through an infinitely small angle from that of each of its neighbors. Since the number of the lines d has indefinitely increased, while both their length and the angles i_2, i_3, etc., have similarly decreased, the above polygon will have become the arc of a circle (see Fig. 5, *b*). The angle subtended will be twice the total angle of twist or $2\ (i_2 + i_3 + \cdot \cdot \cdot) = 2I$.

Throughout the experimental work the rotations stated have been the means of observations in four successive azimuths differing by 45°. The

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[1] The last term represents twice the area included between e and its projection upon the axis.

values of j were therefore j_1, $j_1 + 45°$, $j_1 + 90°$, $j_1 + 135°$. Hence the average value of $\sin 4j$ is zero, and the last term of the above equation for the rotation disappears from the mean. This evidently corresponds to e being perpendicular to the initial axis (Fig. 5, *b*). *The mean rotation, in radians, should therefore equal half the area of the segment of a circle whose angular aperture is twice the angle of twist, and the length of whose arc is the angular difference of phase.* If the twist is increased, the area of the segment, and therefore the rotation will increase much more rapidly because of the increase of the angle subtended and the simultaneous increase in the length of each of the elementary lines which represent the difference of phase in each section, and which together form the length of the arc.

If n_1 and n_2 are the refractive indices of an elementary section and if t is its thickness, and l is the wave-length of the light employed

$$d = 2\pi \frac{(n_2 - n_1)t}{l}.$$

The rotation, being represented by half the area of the segment, is proportional to d^2, and therefore, neglecting variation in n_1 and n_2, should be inversely proportional to the square of the wave-length.

Qualitative Comparison of Theory and Experiments.—The experimental results with rubber-covered jelly cylinders agree with the above theory, for, the torsional rotation is opposite to the twist, varies with the azimuth, is approximately proportional to the inverse square of the wave-length, and increases as a high power of the twist. Leick[1] and the author[2] found the phase difference proportional to the distortion. If, remembering that the arc is equal to the total phase difference, a comparison is made of the distortion of the rubber tubing and the torsional rotation of the contained jelly, the dependence of the rotation upon the length, diameter, and longitudinal compression, will also be found in agreement with this theory.

The double refraction resulting from the distortion of an elliptical cylinder is, however, too complex for exact quantitative comparison between the theory and experimental observations. Therefore simpler forms of distortion were designed, the final one of which will be described.

The jelly was cast as previously described in the two forms of apparatus illustrated in Fig. 2 (*a*) and (*b*). The inside surfaces of the side plates A, A, A', A', were vaselined to prevent any lateral constraint. The length of the helical cylinder (Fig. 2, *a*) between the glass plates was 8 cm., and the portion subjected to transverse strain was 7 cm. The angle between the plates at the beginning and at the end of this distance was 96°. The mean distance between the plates was 1.504 cm. This distance could be varied with great delicacy and precision by the set screws E_1, E_2, etc. The distance between the plates was calculated from outside measurements with a vernier caliper reading to 0.02 mm. For each distance, eight such measurements were made, and eight observations of the rotation in azimuths differing by 45°. The helical cylinder was slipped into a tube which could be rotated in the tray of the polarimeter.

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[1] Ann. d. Phys., XIV. (1904), p. 139.

[2] See below.

The double refraction of the same jelly was determined with the straight cylinder (Fig. 2, *b*). The length of the latter between the glass plates was 7 cm. and the length subjected to strain was 6 cm. The mean distance between the plates A', A', was 1.404 cm. Lateral compression was produced by the set screws E_1', E_2', etc., and measured with a vernier caliper, while the resulting double refraction was deduced from the mean of the displacements of four fringes in a Babinet compensator, sodium light being used.

The observations with jelly No. 78 (which was of the customary composition) are selected as typical. The rotation of the helix and the natural rotation were both ***negative***. The compression produced a ***positive*** rotation, and the artificial rotations given below are the actual rotations less the natural rotation.

TABLE IV.

Rectangular, Helical Cylinder (96°).

Compression	0	.0048	.0100	.0138	.0198	.0238	.0318
Rotation	−17.2°[1]	3.9°	13.3°	35°	57°	70°	89°

As illustrative of the individual observations, the positions of the analyzer for the second compression, and the different azimuths, will be given, namely: 81.9, 83.9, 89.3, 88; 75.2, 76.1, 88, 68.8. Mean = 81.4. The mean position of the analyzer before compression was 68.1 (zero of the instrument = 85.32). Therefore the artificial rotation was 13.3°.

TABLE V.

Straight Rectangular Cylinder.

Compression	0	.006	.0118	.0205	.0397
Mean displacement of fringes	.09	2.0	3.70	5.87	10.30

(Mean distance between fringes = 11.92.)

The abscissas of Fig. 6 are the compressions of the helical cylinder. The points designated by crosses are the mean fringe displacements tabulated above, reduced to the dimensions of the helical cylinder by multiplying by the direct ratio of the lengths and the inverse ratio of the distances between the compressing plates. The circles represent the experimental determinations of the artificial rotation.

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[1] Natural rotation.

Double Refraction of the Jelly.—It should be observed how closely the double refraction, or difference of phase as measured by the displacement of the fringes (dotted line of Fig. 6), is proportional to the compression. The *difference of the refractive indices* for the second compression is

$$n_2 - n_1 = \frac{3.70 \times .0000589}{6 \times 11.92} = 3.04 \times 10^{-6}.$$

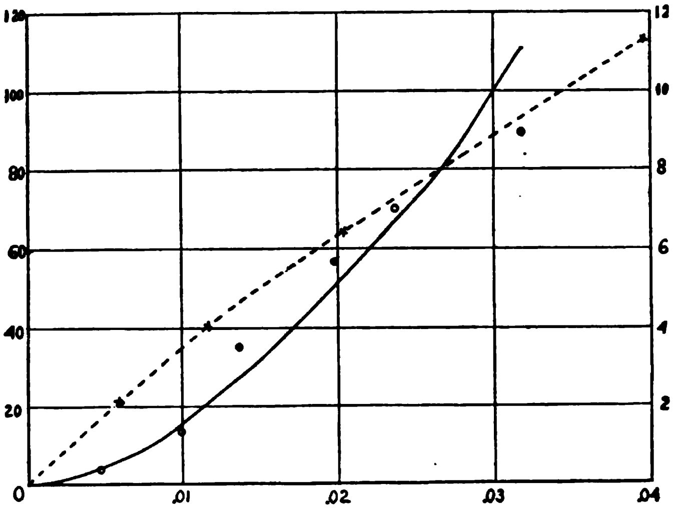

Fig. 6.

Abscissas = compression. Ordinates on left margin = rotation (degrees). Ordinates on right margin (for dotted curve) = displacement of fringes in Babinet compensator.

The difference of the indices for unit compression (the "specific (artificial) double refraction") is

$$\frac{3.04 \times 10^{-6} \times 1.404}{.0118} = 3.63 \times 10^{-4}.$$

This jelly was inclosed on four sides. Leick[1] found 5×10^{-4} for a jelly of nearly the same composition, but inclosed by only the two compressing sides.

Quantitative Comparison of Theory and Experiment.—To calculate the rotation required by the above theory for a compression of .0118, construct (similar to Fig. 5, *b*) a segment of a circle of aperture $2 \times 96°$, the length of whose arc is the total angular difference of phase or (see Fig. 6).

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[1] L. c., p. 148.

$$2\pi\frac{4.04}{11.92} = 2.13.$$

The area of the segment is .72. The artificial rotation is therefore .36 radians, or 20.7°. In this manner the full line of Fig. 6 was constructed.

The writer made nine such series of simultaneous observations of the double refraction and of the artificial rotation. In some cases the jelly was stiffer than the standard and in other cases it was thinner. The proximity of the circles (observed rotation) of Fig. 6 to the full line (calculated rotation) is typical of all nine series. The agreement is not perfect, but, considering the impossibility of making exactly similar surfaces for the helical and the straight cylinders, the relaxation effects which always appeared with the helical cylinder with the highest compressions and consequently reduced the rotation, the fact that errors in the compression were magnified in the rotation (since the rotation is proportional to the square of the compression), and the sensitiveness of the jelly to all disturbances, considering all these difficulties, the agreement between theory and experiment shown by all nine series, of which Fig. 6 is typical, affords conclusive proof of the correctness of the theory.

The glass rods gave no observable rotation for twists up to the breaking point. This is also in agreement with the above theory since the area of a segment of only a few degrees aperture is exceedingly small.

CONCLUSION.

Additional experimental data have been obtained for the artificial rotatory polarization of twisted jelly cylinders, the most important of which are the law of dispersion and the dependence of the rotation upon the distortion of the cross-section. A theory of the phenomena has been developed upon the basis of this distortion. Finally, this theory has been established by the agreement between the rotations observed with cylinders adapted for accurate measurements, and the rotations calculated from the constants of the jelly.

Polytechnic Institute,
Worcester, Massachusetts,
August, 1911.

THE MEASUREMENT OF THE FRICTIONAL FORCE EXERTED ON A SPHERE BY A VISCOUS FLUID, WHEN THE CENTER OF THE SPHERE PERFORMS SMALL PERIODIC OSCILLATIONS ALONG A STRAIGHT LINE.

By George F. McEwen.

THE purpose of the following investigation was to devise a method by which Stokes's law of the frictional resistance of a fluid to the motion of a sphere whose center performs small periodic oscillations could be applied to the measurement of the coefficient of viscosity of fluids. The two main objects were: first, to obtain as close an agreement as possible between the actual working conditions and those demanded by theory; second, to devise a process of measuring the force acting on the sphere, even for fluids having a very large coefficient of viscosity.

The contents of this paper fall under the following five heads:

I. The effect of the internal friction of fluids on the motion of pendulums, from Sir G. G. Stokes's Math. and Phys. Papers, Cambridge, 1880 and 1901, Vols. I. and III.

II. An account of the method adopted in the present investigation to overcome the difficulties mentioned by Stokes, and to more nearly realize in the experimental work the ideal condition assumed in the theory from which Stokes's law was deduced.

III. Experimental tests of the present method.

IV. Suggestions for future research.

V. Summary of the paper.

I. The Effect of the Internal Friction of Fluids on the Motion of Pendulums.

1. *Observations on the Motion of Pendulums.*

An account of the experiments made by Bessel, Baily, Dubuat, and Sabine, and the theoretical results obtained by Poisson, Challis and Plana is given in Stokes's Math. and Phys. Papers, Vol. III., pp. 1–7.

The effect of the surrounding fluid on the time of vibration of a pendulum was computed by Poisson, Challis, Green, and Plana from the hydrodynamical theory of a frictionless fluid. A fair agreement with the observations was found in some cases, but in many cases, especially where the dimensions were small, the theory failed entirely to account for the experimental results.

Because of this failure, Stokes was led to apply the equations of motion[1] of a viscous fluid to pendulum problems.

2. *Stokes's Deduction of the Law of Resistance.*[2]

In 1850 Stokes completed the solution of the following problem:

The center of a sphere performs small periodic oscillations along a straight line; the sphere having a motion of translation only; it is required to determine from the ordinary hydrodynamic equations of motion of a viscous fluid, the motion of the surrounding fluid, and the force exerted on the sphere.

He assumed the velocities to be so small that their squares could be neglected, that there was no slipping of the fluid along the surface of the solid in contact with it, and that the amplitude of vibration of the sphere was very small and remained constant.

His result for the force is

$$F = -A\frac{d^2y}{dt^2} - B\frac{dy}{dt},$$

where y is the displacement and t is the time, and the coefficients A and B have the following values:

$$A = \left(\frac{1}{2} + \frac{9}{4\lambda r}\right) M_1' = K_1' M_1',$$

$$B = \left(\frac{9}{4\lambda r}\right)\left(1 + \frac{1}{\lambda r}\right) M_1' a = K_1'' M_1' a,$$

where M_1' = the mass of the fluid displaced by the sphere,

r = the radius of the sphere,

$a = \frac{2\pi}{T}$, where T is the period of oscillation, $\lambda = \sqrt{\frac{a}{2\mu'}}$, and

μ' = coefficient of viscosity ÷ density.

From the same assumptions and equations, the same result has been obtained by a different method.[3]

For a cylinder oscillating in a direction perpendicular to its axis, Stokes deduced the following expression:

$$F = -K_2' m_2' \frac{d^2y}{dt^2} - K_2'' m_2' a \frac{dy}{dt},$$

where F = the force acting upon unit length of the cylinder, m_2' = the mass of the fluid displaced by unit length of the cylinder, and K_2' and K_2'' are constants depending on the radius of the cylinder, the period of oscillation and μ'.

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[1] Stokes's Math. and Phys. Papers, Vol. I., pp. 75–105.

[2] Stokes's Math. and Phys. Papers, Vol. III., pp. 11–36.

[3] Lamb's Hydrodynamics, edition 3, pp. 583–584.

No simple expressions for K_2' and K_2'' were found that covered all cases, and they are best determined by special series and tables which are given by Stokes in his Math. and Phys. Papers, Vol. III., pp. 47–54. In the same volume he gives a discussion of the conditions upon which the theory from which the above expression was deduced depends.

In the case of the cylinder as well as the sphere, the first coefficient shows that the fluid has the same effect as an increase of the inertia of the system, and the second coefficient shows that the fluid opposes the motion of the system by a force proportional to the velocity.

From observations on the time of vibration the quantity A can be computed, and B can be computed from observations on the arc. Both A and B can be calculated from theory with the aid of Stokes's equations.[1]

3. *The Application of Stokes's Law to the Pendulum Observations of Bessel, Baily and Dubuat.*[2]

By choosing a constant value of μ' Stokes calculated from his theory the periods of a variety of pendulums swinging in air, and the agreement with the values observed by Bessel and Baily was very satisfactory. Only a few observations on the arc of vibration were available, and these were only approximate, in these cases he calculated the decrement of the arc of vibration from his theory, and found as good an agreement with the experiments as could be expected considering the character of the observations. Though most of the observations made on pendulums oscillating in water were also in fair agreement with his theory, there were a number of discrepancies, which he attributed to the experimental methods used.

When a pendulum oscillates in water, or a more viscous liquid, the arc of oscillation rapidly decreases; this diminution forms, in fact, the greatest difficulty in experiments of this kind. This difficulty, which made it impossible to test his theory or to determine the coefficient of viscosity of water or of more viscous liquids by means of a vibrating body, suggested the present investigation.

II. The Method Adopted in the Present Investigation for Measuring the Force Acting on an Oscillating Sphere.

1. *Description of the Apparatus.*

A light rigid bar[3] *FED* is secured to a knife-edge at E, which rests upon a fixed horizontal support. A second bar MN, perpendicular to the first one, carries two movable weights W_3 and W_4; the upper one can be moved to or from E by turning it about the screw EN, and a scale fastened to MN is provided for recording the distance of W_3 from E. The lower weight W_4 can be slid along EM and clamped in any desired position. At F and D (points in line with E) two scale-pans W_1 and W_2 are attached by means of very thin strips of steel. A second light rigid bar ABC is attached by means of similar strips of steel at C and A, to the pan W_2, and to a support above A, which can be given a vertical periodic motion of small amplitude. This support does not touch the apparatus, except at A. The sphere is suspended in the fluid by means of a fine wire, as shown; the wire being attached by a thin steel strip, to a small support B, which can be fastened to the bar AC, in any position between A and C, but is always in line with A and C.

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[1] Stokes's Math. and Phys. Papers, Vol. III., pp. 1–141.

[2] Stokes's Math. and Phys. Papers, Vol. III., pp. 76–140.

[3] See Fig. 1 for a diagram of the apparatus.

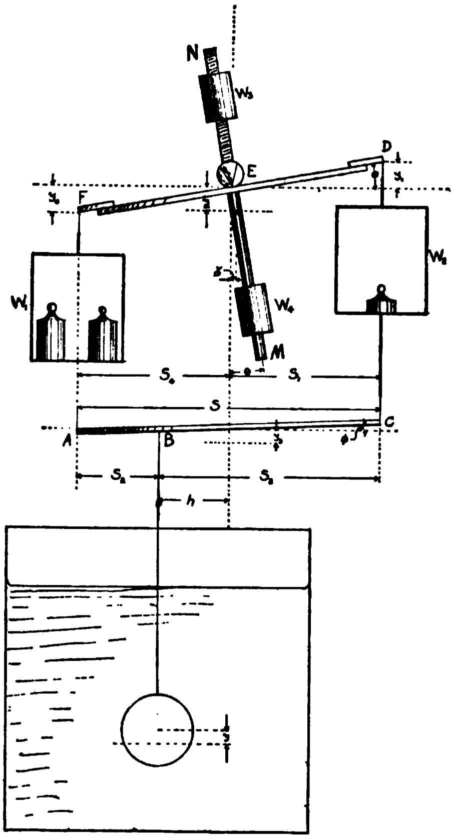

Fig. 1.

By adding weights to the scale-pans, the system can be brought to a state of equilibrium when FD is horizontal. By adjusting the weights W_3 and W_4, the natural period of oscillation can be varied, as this adjustment changes the height of the center of gravity of the system rigidly attached to the knife-edge.

The oscillations will, from the construction of the apparatus, cause the sphere to move in a vertical line, and if the support of A is fixed, these oscillations will subside because of the friction. But if the support of A is given a vertical periodic motion, the system will be set in forced vibration, and the amplitude, phase and period of this forced vibration will depend upon the amplitude, phase and period of the motion of the support, for any given adjustment of the vibrating system.

2. *The Theory of the Forced Vibrations of the Above System.*

Explanation of the Symbols:

M'' equals the mass rigidly connected to the knife-edge E.

I_C'' equals the moment of inertia of M'' about C_1.

I_E'' equals the moment of inertia of M'' about E.

C_1 is the center of mass of M''.

EC_1 equals l.

m_3' equals the mass of the lower bar.

I_3' equals the moment of inertia of m_3' about its center of mass.

y_3 equals the displacement of the center of mass of m_3' from the position of equilibrium.

M_1 equals the mass of the sphere and its suspending wire.

θ equals the angular displacement of FD from its equilibrium position which is assumed to be horizontal.

M_1' equals the mass of the fluid displaced by the sphere.

g equals the acceleration of gravity

$s = s_2 + s_3$; $h = \frac{2}{s} - s_2$.

θ_0 equals the angular displacement of the heavy pendulum used to maintain the vibrations.

$-l_1\theta_0$ equals y_0, the linear displacement of the point A.

β equals the change in torque due to the elasticity of one suspending strip when bent through unit angle.

$\beta_1 y$ equals the change in the force on the wire holding the sphere, due to the elasticity of the surface film of the liquid, and to the varying length of the wire immersed.

The variable force exerted on the sphere by the fluid equals

$$-A\frac{d^2y}{dt^2} - B\frac{dy}{dt}$$

Denote the variable force exerted on the wire by the fluid by:

$$-A'\frac{d^2y}{dt^2} - B'\frac{dy}{dt} + \beta_1 y.$$

ϕ equals the angular displacement of the lower bar from the equilibrium position.

$-k_2\frac{d\phi}{dt}$ = the torque on the lower bar due to the friction of the air and the suspending wires.

$-k_1\frac{d\theta}{dt}$ = the torque on the upper bar due to the friction of the air, the suspending wires, and the knife-edge.

F_E' equals the horizontal force at E acting on the knife-edge.

F_E equals the vertical force at E acting on the knife-edge.

F_A equals the vertical force at A acting on the lower bar.

$- F_B$ equals the vertical force at B acting on the lower bar.

F_C equals the vertical force at C acting on the lower bar.

$- F_D$ equals the vertical force at D acting on the upper bar.

$- F$ equals the vertical force at F acting on the upper part.

m_3 equals the mass of each scale-pan and contents, and wires between C and D.

m_4 equals the mass of each scale pan and contents, and wires attached at F.

The meaning of the other symbols used is indicated on the diagram of the apparatus.

Fundamental Dynamical Relations:

$$M_1\frac{d^2y}{dt^2} = F - M_1g + M_1'g - (A + A')\frac{d^2y}{dt^2} - (B + B')\frac{dy}{dt} + \beta_1 y,$$

$$m_3'\frac{d^2y_3}{dt^2} = - F_B + F_A + F_C - m_3'g,$$

$$I_3'\frac{d^2\phi}{dt^2} = F_C\frac{S}{2} - F_A\frac{S}{2} + F_Bh - 3\beta\phi - k_2\frac{d\phi}{dt},$$

$$m_3\frac{d^2y_1}{dt^2} = F_D - F_C,$$

$$\begin{aligned}I_C''\frac{d^2\theta}{dt^2} = &- F_DS_1 + FS_4 - F_E'L\cos\theta - F_EL\sin\theta - k_1\frac{d\theta}{dt} - 2\beta\theta\\ &+ FL\sin\theta + F_Dl\sin\theta,\end{aligned}$$

$$M''\frac{d^2y}{dt^2} = M''\left\{(\cos\theta)\left(\frac{d\theta}{dt}\right)^2 + (\sin\theta)\frac{d^2\theta}{dt^2}\right\}l = F_E - F - F_D - M''g,$$

$$M''\frac{d^2x}{dt^2} = M''\left\{(\cos\theta)\frac{d^2\theta}{dt^2} - (\sin\theta)\left(\frac{d\theta}{dt}\right)^2\right\}l = F_E',$$

$$m_2\frac{d^2y_4}{dt^2} = F - m_2g,$$

$$\begin{aligned}I_C''\frac{d^2\theta}{dt^2} = S_4\left(m_2\frac{d^2y_4}{dt^2} + m_2g\right) - S_1\left\{F_C + m_3\frac{d^2y_1}{dt^2}\right\} - k_1\frac{d\theta}{dt} - 2\beta\theta\\ - M''l^2(\cos\theta)\left\{(\cos\theta)\frac{d^2\theta}{dt^2} - (\sin\theta)\left(\frac{d\theta}{dt}\right)^2\right\}\\ - l(\sin\theta\left\{M''l\left[(\cos\theta)\left(\frac{d\theta}{dt}\right)^2 + (\sin\theta)\frac{d^2\theta}{dt^2}\right] + M''g\right\}.\end{aligned}$$

Fundamental Kinematical Relations:

$\underline{x}$ and $\underline{y}$ are the coördinates of C_1,

$$\underline{x} = l\sin\theta, \qquad \underline{y} = -l\cos\theta,$$

$$\frac{d\underline{x}}{dt} = l(\cos\theta)\frac{d\theta}{dt}, \quad \frac{d\underline{y}}{dt} = l(\sin\theta)\frac{d\theta}{dt},$$

$$\frac{d^2\underline{x}}{dt^2} = l\left\{(\cos\theta)\frac{d^2\theta}{dt^2} - (\sin\theta)\left(\frac{d\theta}{dt}\right)^2\right\},$$

$$\frac{d^2\underline{y}}{dt^2} = l\left\{(\sin\theta)\frac{d^2\theta}{dt^2} + (\cos\theta)\left(\frac{d\theta}{dt}\right)^2\right\},$$

$$y_1 = S_1\theta, \qquad \frac{dy_1}{dt} = S_1\frac{d\theta}{dt}, \qquad \frac{d^2y_1}{dt^2} = S_1\frac{d^2\theta}{dt^2},$$

$$y_4 = -S_4\theta, \quad \frac{dy_4}{dt} = -S_4\frac{d\theta}{dt}, \quad \frac{d^2y_4}{dt^2} = -S_4\frac{d^2\theta}{dt^2},$$

$$y = \frac{1}{S}(S_3y_0 + S_2y_1) = \frac{1}{S}(-S_3l_1\theta_0 + S_2S_1\theta),$$

$$y_3 = \tfrac{1}{2}(y_0 + y_1), \quad y_0 = -l_1\theta_0,$$

$$\phi = -\left(\frac{y_0 - y_1}{S}\right) = \frac{1}{S}(l_1\theta_0 + S_1\theta),$$

$$\frac{dy}{dt} = \frac{1}{S}\left(S_1S_2\frac{d\theta}{dt} - S_3l_1\frac{d\theta_0}{dt}\right),$$

$$\frac{d^2y}{dt^2} = \frac{1}{S}\left(S_1S_2\frac{d^2\theta}{dt^2} - S_3l_1\frac{d^2\theta_0}{dt^2}\right),$$

$$\frac{dy_3}{dt} = \frac{1}{2}\left(S_1\frac{d\theta}{dt} - l_1\frac{d\theta_0}{dt}\right),$$

$$\frac{d^2y_3}{dt^2} = \frac{1}{2}\left(S_1\frac{d^2\theta}{dt^2} - l_1\frac{d^2\theta_0}{dt^2}\right),$$

$$\frac{d\phi}{dt} = \frac{1}{S}\left(l_1\frac{d\theta_0}{dt} + S_1\frac{d\theta}{dt}\right),$$

$$\frac{d^2\phi}{dt^2} = \frac{1}{S}\left(l_1\frac{d^2\theta_0}{dt^2} + S_1\frac{d^2\theta}{dt^2}\right).$$

The above dynamical and kinematical relations can be so combined as to give the following ordinary differential equation:

$$P\frac{d^2\theta}{dt^2} + P_1\frac{d\theta}{dt} + P_2\theta = P''\frac{d^2\theta}{dt^2} + P'\frac{d\theta_0}{dt} + \underline{P}_2\theta_0,$$

in which the coefficients are constants and have the following values:

$$P = \left[I_E'' + m_2S_4^2 + m_3S_1^2 + \frac{S_1^2S_2^2}{S^2}(M_1 + A + A') + \frac{S_1^2}{4}m_3' + I_3'\frac{S_1^2}{S^2}\right],$$

$$P_1 = \left[\frac{S_1^2S_2^2}{S^2}B + \left\{\frac{S_1^2S_2^2}{S^2}B' + k_1 + k_2\left(\frac{S_1}{S}\right)^2\right\}\right],$$

$$P_2 = \left[M''gl + \beta\left(2 + 3\left[\frac{S_1}{S}\right]^2\right) - \frac{S_1^2S_2^2}{S^2}\beta_1\right],$$

$$P'' = \left[\frac{l_1S_1S_2S_3}{S^2}(M_1 + A + A^1) + \frac{l_1S_1}{4}m_3' - \frac{l_1S_1}{S^2}I_3'\right],$$

$$P' = \left[(B + B')\frac{l_1S_1S_2S_3}{S^2} - \frac{l_1S_1}{S^2}k_2\right],$$

$$\underline{P}_2 = -\left[\frac{3l_1S_1\beta}{S^2} + \frac{l_1S_1S_2S_3}{S^2}\beta_1\right].$$

Assume

$$y_0 = ce^{-\alpha t}\sin at = -l_1\theta_0,$$

and substitute in the second member of the differential equation; the result will be:

$$P\frac{d^2\theta}{dt^2} + P_1\frac{d\theta}{dt} + P_2\theta = P_0''\left(-\frac{c}{l_1}\right)e^{-\alpha t}\sin at + P_0'\left(-\frac{c}{l_1}\right)e^{-\alpha t}\cos at,$$

where

$$P_0'' = (\underline{P}_2 - [a^2 - \alpha^2]P'' - \alpha P'), \quad \text{and} \quad P_0' = a(P' - 2\alpha P'').$$

Assume that the following ordinary equation is a particular integral of the differential equation:

$$\theta = A_1e^{-\alpha t}\sin(at - \theta_1) + B_1e^{-\alpha t}\cos(at - \theta_2),$$

substitute in the equation and solve for the quantities:

$$A_1,\ \theta_1,\ B_1,\ \text{and}\ \theta_2.$$

The following values of the constants will make the assumed form for θ, a solution:

$$A_1 = \frac{P_0''(\sec\theta_1)\left(-\frac{c}{l_1}\right)}{P_2 + P[\alpha^2 - a^2] - \alpha P_1 + (P_1a - 2a\alpha P)\tan\theta_1},$$

$$B_1 = \frac{P_0'(\sec\theta_2)\left(-\frac{c}{l_1}\right)}{P_2 + P[\alpha^2 - a^2] - \alpha P_1 + (P_1a - 2a\alpha P)\tan\theta_2},$$

$$\tan\theta_1 = \frac{P_1a - 2a\alpha P}{P_2 + P[\alpha^2 - a^2] - \alpha P_1}.$$

To obtain the complete integral of the equation, the complementary function, $A_3e^{-P_1t/2P}\sin(\beta_3t+\theta_3)$ would have to be added to the above value of θ. A_3 and θ_3 are arbitrary constants, depending for their values on how the system is started, and

$$\beta_3=\frac{\sqrt{4P_2P-P_1^2}}{2P}.$$

In the present method of measurement, no observations are taken until the complementary function has a negligible value, so only the first or particular integral will be retained.

In practical applications, the ratio of the maximum value of θ to the maximum value of θ_0 is determined by experiment. The relation of the coefficient B to that ratio, which is required for determining B will now be derived. The following equation for θ_0 is assumed:

$$\theta_0=-\frac{c}{l_1}e^{-at}\sin at.$$

Then the expression for θ can be reduced to the form

$$\theta=A_2e^{-at}\sin(at-\theta_1+\theta_3)$$

where

$$A_2=\sqrt{A_1^2+B_1^2},\quad\text{and}\quad\tan\theta_3=\frac{B_1}{A_1}=\frac{P_0'}{P_0''}.$$

Let t_1 be the time at which θ has a maximum value, and t_2 be the time at which θ_0 first reaches its maximum value after t_1. Let $t_2-t_1=\Delta t$.

By taking the first derivative of θ and θ_0, the maximum values, θ' and θ_0' given below are obtained:

$$\theta'=A_2e^{-at_1}\left(\frac{1}{\sqrt{1+\left(\frac{\alpha}{a}\right)^2}}\right),\quad\theta_0'=-\frac{c}{l_1}e^{-at_2}\left(\frac{1}{\sqrt{1+\left(\frac{\alpha}{a}\right)^2}}\right).$$

Dividing the first equation by the second gives

$$\frac{\theta'}{\theta_0'}=R'=e^{a\Delta t}\left(\frac{A_2}{-\frac{c}{l_1}}\right).$$

This ratio is obtained experimentally by first observing the maximum value of θ, then observing the next maximum value of θ_0, and dividing the first by the second. Substituting the value of A and B in the expression for A gives

$$A_2=-\left(\frac{c}{l_1}\right)\frac{\sqrt{(P_0')^2+(P_0'')^2}}{\sqrt{(P_2+P[\alpha^2-a^2]+\alpha P_1)^2+(P_1a-2a\alpha P)^2}},$$

and

$$R' = e^{a\Delta t}\frac{\sqrt{(P_0')^2 + (P_0'')^2}}{\sqrt{(P_2 + P[\alpha^2 - a^2] - \alpha P_1)^2 + (P_1 a - 2a\alpha P^2)}}.$$

This expression shows that R' is independent of the amplitude of the vibration, but is a function of the constant coefficients of one of the preceding differential equations.

3. *The Deduction of a Practical Working Formula from the Above Theory.*

It appears that P_2 is the constant by which θ is multiplied to obtain that part of the torque which opposes the displacement of the system, but does not depend on the friction. In the expression

$$P_2 = M''gl + \beta\left(2 + 3\left[\frac{S_1}{S}\right]^2\right) - \frac{S_1^2 S_2}{S^2}\beta_1$$

l is the distance above E of the center of mass of the system rigidly attached to the knife-edge. As will be seen by referring to the expression for R', for the values of the constants in the expression for R', the quantity l appears only in the expression for P_2. Therefore, by shifting the weight W_3, l and consequently $M''gl$ can be changed without affecting the remainder of the expression for R'.[1]

Let

$$R = e^{-a\Delta t}R' = \frac{\sqrt{(P_0')^2 + (P_0'')^2}}{\sqrt{(P_2 + P[\alpha^2 - a^2] - \alpha P_1)^2 + (P_1 a - 2a\alpha P)^2}},$$

now if R is measured for three different values of $M''gl$, there will be three equations from which P_1 can be computed by eliminating the other unknown quantities.

Suppose $M''gl$ is changed by raising or lowering the weight W_3, a known amount; the amount due to one complete turn, for example. Denote this change by $\sqrt{z_2}$. Then

$$M''l = (M'' - W_3)\underline{l} + W_3 l_3,$$

where l is the distance of the center of the mass of M'' from E, $\underline{l}$ is the distance of the center of mass of $(M'' - W_3)$ from E, and l_3 is the distance of the center of mass of W_3 from E. Let the change in l_3 be Δl_3, and denote the corresponding change in l by Δl, then $\underline{l}$ will remain the same as it depends only on that part of the mass whose position with reference to E is fixed. Therefore,

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[1] Changing l in this way would produce a known small change in P, which can be easily compensated for by changing the weights in the scale-pans W_1 and W_2. It will be assumed that this is done, and therefore P will be treated as a constant.

$$M''(l+\Delta l) = (M''-W_3)l + W_3(l_3+\Delta l_3),$$

$$\Delta l = \frac{W_3}{M''}\Delta l_3,$$

and

$$\sqrt{z_2} = M''g\Delta l = W_3 g \Delta l_3.$$

In the equation for R, denote the numerator by $\sqrt{z_3}$, denote $(aP_1-2a\alpha P)^2$ by z_1, denote $(P_2+P[\alpha^2-a^2]-\alpha P_1)$ by $n\sqrt{z_2}-z'$,[1] and let $+\frac{z'}{\sqrt{z_2}}=w$. Then

$$(P_2+P[\alpha^2-a^2]-\alpha P_1) = \sqrt{z_2}(n-w),$$

and the equation for R takes the following simplified form:

$$R_n^2 = \frac{z_3}{z_2(n-w)^2+z_1}.$$

Now by varying n, the number of complete turns of W_3, R_n will vary but z_2, z_3, and z_1 will remain constant, and are positive. w is a constant, positive or negative, and depends on the position of W_3 when n is assumed to be zero.

The maximum value of R, denoted by R_w is:

$$R_w = \sqrt{\frac{z_3}{z_1}},$$

therefore R_w is a function of z_1 and z_3 only, and corresponds to the special case when there is resonance. The above equation involving R_n can be written in the following forms:

$$(n-w)^2 + V\left[1-\left(\frac{R_w}{R_n}\right)^2\right] = 0,$$

$$(n-w) = \pm\sqrt{V}\sqrt{\left(\frac{R_w}{R_n}\right)^2-1} = \pm\frac{\sqrt{V}}{R_n}\sqrt{R_w^2-R_n^2},$$

$$R_w = R_n\sqrt{1+\frac{(n-w)^2}{V}}, \quad \sqrt{V} = \frac{\pm(n-w)R_n}{\sqrt{R_w^2-R_n^2}},$$

where $V=\frac{z_1}{z_2}$.

An inspection of the above equations shows that if R_n and R_w are both multiplied by an arbitrary constant, the roots of the equation will be unaltered. Therefore the ratios used need only be proportional to the true values of the ratios. Also, if (A) has a constant amplitude, only the readings for θ need to be taken.

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[1] Assume that Δl_3 corresponds to one turn of W_3, and denote by n the number of turns from a given position near the top of the screw. Then n and P_2 increase as W_3 is lowered.

From three observations, three correspondeing values of n and R_n can be obtained, and the two quantities R_w and w, which will be the same in all cases can be eliminated, thus giving the value of $\sqrt{V}$.

Now,

$$\sqrt{z_1} = \sqrt{V}\sqrt{z_2} = aP_1 - 2a\alpha P,$$

and therefore

$$P_1 = \sqrt{V}\sqrt{\frac{z_2}{a^2}} + 2\alpha P,$$

also

$$P_1 = B\left(\frac{s_1s_2}{s}\right)^2 + \left\{B'\left(\frac{s_1s_2}{s}\right)^2 + k_1 + k_2\left(\frac{s_1}{s}\right)^2\right\},$$

$$B = \left(\frac{s}{s_1s_2}\right)^2\sqrt{V}\sqrt{\frac{z_2}{a^2}} + 2\alpha P - \left(\frac{s}{s_1s_2}\right)^2\left\{B'\left(\frac{s_1s_2}{s}\right)^2 + k_1 + k_2\left(\frac{s_1}{s}\right)^2\right\},$$

and

$$B = \left(\frac{s}{s_1s_2}\right)^2\sqrt{V}\sqrt{\frac{z_2}{a^2}} - K,$$

where K is a positive constant, and depends only on s, s_1, s_2, α, P and the friction not due to the sphere. Therefore, if two different spheres of radii r_1 and r_2 are used,

$$B_1 = \left(\frac{s}{s_1s_2}\right)^2\sqrt{V_1}\sqrt{\frac{z_2}{a^2}} - K_1,$$

and

$$B_2 = \left(\frac{s}{s_1s_2}\right)^2\sqrt{V_2}\sqrt{\frac{z_2}{a^2}} - K_2,$$

where $K_2 - K_1$ is practically zero. Therefore, subtracting the first from the second gives

$$B_2 - B_1 = (\sqrt{V_2} - \sqrt{V_1})\sqrt{\frac{z_2}{a^2}}\left(\frac{s}{s_1s_2}\right)^2.$$

From this equation, the difference between B_2 and B_1 can be found, since all the quantities in the second member can be measured. From the theory given by Stokes, this difference has the following value:

$$B_2 - B_1 = 3\pi\sqrt{2a}\sqrt{\mu'}\left\{(r_2 - r_1)\left(r_2 + r_1 + \sqrt{\frac{a}{2}}\sqrt{\mu'}\right)\right\}\rho,$$

and from this equation μ the coefficient of viscosity can be computed. But the vessel containing the liquid must be large enough, compared to the sphere used so that the assumption on which the equations were derived are justified, or a correction for the effect of the containing vessel must be made.

Let B_1' and B_2' be the values of B_1 and B_2 corresponding to a vessel of infinite radius. Let λ_1 and λ_2 be coefficients depending on a, μ', and the ratio of the radius of the sphere to the containing vessel, so that

$$\lambda_1 B_1' = B_1,$$

and

$$\lambda_2 B_2' = B_2,$$

then

$$\lambda_2 B_2' - \lambda_1 B_1' = (\sqrt{V_2} - \sqrt{V_1}) \sqrt{\frac{z_2}{a^2}} \left(\frac{s}{s_1 s_2} \right)^2.$$

Let λ_1'' and λ_2'' correspond to the cases where the radius of the vessel is R'' and R' respectively; the same sphere being used. Then

$$B_1'(\lambda_1'' - \lambda_1') = (\sqrt{V_1''} - \sqrt{V_1'}) \sqrt{\frac{z_2}{a^2}} \left(\frac{s}{s_1 s_2} \right)^2.$$

If this result is zero, then the radius is large enough, and no correction is necessary.

III. Experimental Results.

A gravity pendulum consisting of a wrought iron rod 1.5 cm. in diameter, and 180 cm. in length; and two cylindrical weights, each being of 5 kg. mass, was mounted on a frame supported by two concrete piers. By adjusting the position of the weights, any value of the period, from about 2 to 25 seconds could be secured. By means of a mirror attached to the knife-edge, and a vertical scale and horizontal telescope supported on one of the piers, 115 cm. from the mirror, measurements of the angular displacements were made. The scale was divided into mm., and readings were taken to 0.1 mm. Within the limits of observational errors, the displacement of the pendulum agreed with the following formula:

$$\theta_0 = \left(-\frac{c}{l_1} \right) e^{-\alpha t} \sin at.$$

The measuring apparatus, already described, was supported with its knife-edge E parallel to that of the large pendulum,[1] and about 8 cm. above it. A mirror was attached to E above the mirror of the large pendulum, and a second horizontal telescope was mounted above that used for the large pendulum. The same scale was used for both. The apparatus was not enclosed nor shielded from air currents.

A short rigid bar, secured to the large pendulum in a position perpendicular to its knife-edge and pendulum rod, supported at the distance l_1

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[1] See Fig. 2 for diagram.

from the knife-edge, by means of a fine wire, the end *A* of the lower beam of the measuring apparatus. Because of this arrangement, the end *A* of the beam *AC* was constrained to have the vertical displacement:

$$y_0 = -l_1\theta_0 = ce^{-\alpha t}\sin at.$$

In order to test the capacity of the apparatus for measuring large forces acting on the sphere, dark filtered cylinder oil, grade "N," was used at temperatures from 18° to 22° Cent. At these temperatures, the coefficient of viscosity of the oil is several thousand times as great as that of water.

The numerical values of the constants in the experiment on oil are tabulated below:

Weight of the measuring apparatus, about	400 grams.
Weight in each scale-pan, about	80 grams.
Weight of each scale-pan, about	15 grams.

$W_3 = 13.52$ gr. $M'' = 76.84$ gr.

$\Delta l_3 = 00.0794$ cm. $\sqrt{z_2} = 1{,}052$ dyne cm.

$s_1 = 5.0$ cm. $s_2 = 2.5$ cm.

$s_3 = 7.5$ cm. $s = 10.0$ cm.

$a = 1.702$ (sec.)$^{-1}$. $\alpha = 0.0007$ (sec.)$^{-1}$.

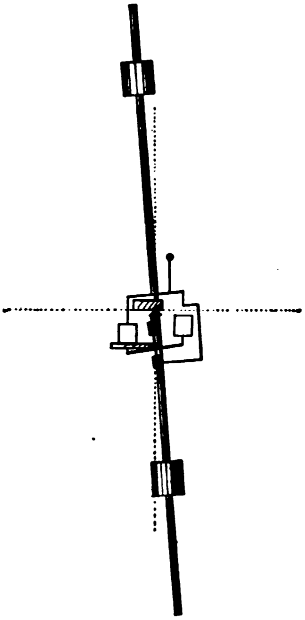

Fig. 2.

The radius of the cylinder containing the liquid was 5.5 cm.; its depth was 18 cm. The cylinder was practically full of the liquid, and in all cases the top of the sphere was 6.5 cm. below the liquid surface. The maximum velocity of the sphere was less than 0.1 cm./sec., and itsmaximum displacement was less than 0.07 cm.

The maximum deflections θ' and θ_0' were determined alternately, and the value for θ' was divided by the mean of the two nearest values of θ_0' for a single determination of the ratio R'. The following set of readings and results is typical of the accuracy of the work. In the first and second columns are the average of the differences of the scale readings for determining θ_0' and θ_0 respectively. The last column contains the average value of R' minus each value.

		R'	$.5692-R'$			R'	$.5692-R'$
2.590	1.560	.6025	−.0063	2.445	1.460	.5970	−.0008
2.575	1.520	.5910	.0048	2.425	1.460	.6062	−.0058
2.560	1.510	.5900	.0062	2.400	1.430	.5960	.0002
2.540	1.505	.5925	.0037	2.370	1.420	.5980	−.0018
2.515	1.495	.5945	.0017			.5962	
2.480	1.485	.5990	−.0028				

Tabulation of Results.—The temperature of the liquid is denoted by t. Under $\sqrt{V}$ are the results of substituting the given values of n, w, R_n, and R_w in the formula:

$$\sqrt{V} = \frac{\pm (n - w)}{\sqrt{R_w{}^2 - R_n{}^2}}.$$

$t = 18.1°$ $r_1 = .495$ cm. $R_w{}^2 = 8.30$ $w = 1.384$.

n	R_n	$R_n{}^2$	$\sqrt{V_1}$	$B_1+K=395.7\sqrt{V_1}$
1	2.612	6.822	2.973	
7	1.5513	2.4065	2.950	
11	.9375	.8789	2.965	
17	.5709	.3259	2.954	
			2.960	1,171

$t = 18.05°$ $r_2 = .792$ cm. $R_w{}^2 = 10.12$ $w = -1.700$.

n	R_n	$R_n{}^2$	$\sqrt{V_2}$	$B_2+K=395.7\sqrt{V_2}$
0	3.123	9.755	8.79	
6	2.392	5.722	8.78	
18	1.296	1.680	8.79	
			8.787	3,477

$t = 22.3°$ $r_1 = .495$ cm. $R_w{}^2 = 11.30$ $w = 2.98$.

n	R_n	$R_n{}^2$	$\sqrt{V_1}$	B_1-K
1	1.9817	3.927	1.445	
7	1.1335	1.2848	1.436	
11	.5792	.33507	1.405	
17	.3423	.11717	1.436	
			1.431	566

$t = 22.15°$ $r_2 = .792$ cm. $R_w{}^2 = 9.34$ $w = 1.50$.

n	R_n	$R_n{}^2$	$\sqrt{V_2}$	B_2-K
0	2.755	7.590	3.125	
6	1.748	3.055	3.137	
12	.9001	.8102	3.237	
18	.5701	.3255	3.136	
			3.159	1,249

$t = 22.10°$ $r_2 = .792$ cm. $R_w^2 = 8.63$ $w = 1.73$.

n	R_n	R_n^2	$\sqrt{V_2}$	B_2+K
1	2.862	8.191	3.155	
7	1.513	2.289	3.142	
11	.9500	.9025	3.160	
17	.5962	.3555	3.162	
			3.155	1,248

The coefficient of viscosity was not computed from the preceding data, because the cylinder was not large enough compared to the spheres for the assumption of a cylinder of infinite radius to be valid for a fluid having such a large coefficient of viscosity. However, the above trials show that the method adopted can be successfully applied, even to the measurement of very large frictional forces.

The apparatus, used in the experiment just described, was not well adapted to the measurement of small forces acting on the sphere, because of its crudeness, and because the friction in the apparatus itself was comparatively large. But in order to test the method through a wide range of conditions, an attempt was made to determine the coefficient of viscosity of water. In this experiment the sphere was suspended close to the point C of the lower bar, in order to increase the effect of the frictional force. Also, since the quantity z_1 was now much smaller than before, the series of values of R was obtained by correspondingly smaller changes in the expression $(P_2 + P[\alpha^2 - a^2] - \alpha P_1)$. The changes were made by adding equal weights to each scale-pan, thus, varying P instead of P_2 as was done before; and by a method similar to that already described the following formula was derived:

$$(n - w)^2 + V\left[1 - \left(\frac{R_w}{R_n}\right)^2\right] = 0,$$

in which n is the number of multiples of a given weight W_4 added to each scale-pan, $\sqrt{z_2}$ equals the change in the moment of inertia of the system when one of these weights is added to each pan. That is:

$$\sqrt{z_2} = a^2W_4(s_1^2 + s_4^2).$$

In this case a decrease in n has the same effect as an increase in the previous case, but this formula can be used in the same way as the previous one, assuming the symbols to have the values indicated above.

The numerical values of the constants in the following experiment are tabulated below:

Weight of the measuring apparatus, about 400 grams.

Weight in each scale-pan, about 50 grams.

Weight of each scale-pan, about 15 grams.

$W_4 = 1.00$ grams. $\sqrt{z_2} = 146.5$ dyne cm.

$s_1 = 5.0$ cm. $s_2 = 8.90$ cm.

$s_3 = 1.1$ cm. $s = 10.0$ cm.

$\rho = 1.000$. $a = 1.711$ (sec.)$^{-1}$.

The radius of the cylinder containing the liquid was 8 cm.; its depth was 20 cm. The cylinder was practically full of water, and in each case the top of the sphere was 6.5 cm. below the surface of the water. The maximum velocity of the sphere was less than .15 cm./sec., and its maximum displacement was less than .09 cm.

The amplitude of the large pendulum was maintained constant by means of an electro-magnet and the scale readings for determining θ were taken as before. In this case they should be constant. The following set of readings and results is typical of the accuracy of the work. The differences between successive scale readings, denoted by R, are given in the first column. The last column contains the average value of R minus each value.

R	$2.719-R$	R	$2.719-R$	R	$2.719-R$
2.67	+.049	2.74	−.021	2.68	+.039
2.70	+.019	2.73	−.011	2.67	+.049
2.68	+.039	2.68	+.039	2.68	+.039
2.69	+.029	2.69	+.029	2.71	+.009
2.68	+.039	2.72	−.001	2.76	−.041
2.72	−.001	2.73	−.011	2.76	−.041
2.79	−.071	2.69	+.029	2.78	−.061
2.77	−.051	2.72	−.001	2.71	+.009
2.78	−.061	2.71	+.009	2.75	−.031
2.77	−.051	2.71	+.009	2.70	+.019
2.72	−.001	2.70	+.019	Aver. R 2.719	
2.72	−.001				

Tabulation of Results.

The temperature of the liquid is denoted by t. Under $\sqrt{V}$ are given the results of substituting the values of n, w, R_n, and R_w in the formula:

$$\sqrt{V} = \frac{\pm (n - w)R_n}{\sqrt{R_w^2 - R_n^2}}.$$

$t = 16.5^\circ \quad r = .495$ cm. $\quad R_w^2 = 85.8 \quad w = 3.474.$

n	R_n	R_n^2	$\sqrt{V_1}$	$B_1 + K = 2.525\sqrt{V_1}$
4	6.994	48.95	.6057	
2	3.525	12.42	.6065	
0	1.593	2.538	.6065	
			.606	1.530

$t = 16.5^\circ \quad r_2 = .952$ cm. $\quad R_w^2 = 42.80 \quad w = 4.34.$

n	R_n	R_n^2	$\sqrt{V_2}$	$B_2 + K = 2.525\sqrt{V_2}$
8	1.850	3.422	1.079	
4	6.238	38.92	1.080	
2	2.721	7.405	1.070	
0	1.556	2.420	1.064	
			1.073	2.710

$$B_2 - B_1 = 2.710 - 1.530 = 1.18.$$

The expression $(B_2 - B_1)$ can be transformed into the following:

$$B_2 - B_1 = 3\pi\sqrt{2a}\sqrt{\mu'}\left\{(r_2 - r_1)\left(r_2 + r_1 + \sqrt{\frac{2}{a}}\sqrt{\mu'}\right)\right\},$$

from which after substituting the values from the above experiment, the following equation for determining μ is obtained:

$$1.18 = 3\pi\sqrt{3.422}\sqrt{\mu'}\{(.457)(1.447 + 1.08\sqrt{\mu'})\}$$

or

$$\mu' = 1.338\sqrt{\mu'} - .1369 = 0.$$

The solution of this equation gives $\mu = .0091$, while the value .0111 is given by the formula:[1]

$$\mu = \frac{.0178}{1 + .0337t + .000221t^2}.$$

Thus there is a fair agreement with other methods, considering the unfavorable working conditions.

IV. SUGGESTIONS FOR FUTURE RESEARCH.[2]

In the measuring apparatus used in the experiments just described, the force which opposed the displacement of the system but did not depend upon the friction, was due partly to the elasticity of the steel strips and partly to gravity. If, instead of steel strips knife-edges were used, the return force would depend upon gravity only and could be made so small, without loss of stability, that a given natural period could be secured by a much lighter apparatus. If, in addition to reducing the weight, agate bearings were provided, the friction of the apparatus would be greatly reduced, and therefore greater accuracy would result. It would also be desirable to protect the apparatus from air currents and dust.

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[1] This formula is based on Poiseuilles' capillary tube experiment. See Lamb's Hydrodynamics, 3d edition, p. 536.

[2] Further suggestions for future research are given in Stokes's Math. and Phys. Papers, Vol. III., pp. 123–127.

In making measurements, the weight W_3 should be so adjusted that two values of the ratio R are roughly one half the maximum value, one corresponding to the case where $(P_2 + P[\alpha^2 - a^2] - \alpha P_1) = \sqrt{z_2}(n - w)$ is positive and the other when it is negative, and the third value should be near the maximum. The three values of R thus obtained are sufficient for computing the force, but it is desirable to check the work by additional values of R between the first two.

The same apparatus can be used for the measurement of the force acting on any vibrating body, if the force opposes the displacement and is proportional to the velocity, and it is well adapted to the case in which a very small maximum velocity and displacement is required.

The advantages of measuring the coefficient of viscosity by the oscillating sphere method can only be settled by a series of experiments in which the force is measured when the working conditions are in agreement with those required by the theory.

V. Summary of the Paper.

The hydrodynamical theory of a frictionless fluid failed to account for the experimental results of the pendulum observations of Bessel, Baily and Dubuat, and this fact led Stokes to apply the theory when the fluid friction was taken into account.

The predictions based on this theory agreed well with the experiments on pendulums vibrating in gases, but when the fluid was water, instead of gas, the agreement was not very satisfactory. This disagreement was due to the difficulty of making the observations, rather than to the theory.

The fact that the inertia correction could be determined experimentally and that it had been shown how it depended on the coefficient of viscosity led Stokes to suggest that his theory might be employed to calculate the coefficient of viscosity of gases from observations on a pendulum, consisting either of a sphere attached to a fine wire, or of a cylinder.

He also showed how to compute the frictional force acting on a sphere and a cylinder, vibrating in a viscous fluid. From this result the coefficient of viscosity can be computed from observations which give the retarding force. For this purpose he proposed that the decrement of the arc of oscillation be used. This does not require as accurate a value of the period as the other method.

The greatest difficulty in each method when the coefficient of viscosity is as large as that of water, or larger, is the rapidity with which the oscillations diminish.

The present investigation was undertaken to overcome the difficulties mentioned by Stokes when applying the oscillating sphere method to the measurement of large coefficients of viscosity. This object was accomplished by employing a forced vibration method in which the sphere was suspended by a fine wire, and had a slow motion of translation only along a vertical line, and the oscillations were small, and either diminished very slowly, or were maintained constant for any desired length of time.

The above method was applied to the measurement of the force acting on a sphere in water and in a very viscous oil. In each case a satisfactory measurement of the force was obtained.

It is assumed in the hydrodynamical theory that the velocities and displacements are very small, that the amplitude remains constant, and that there is no rotation of the sphere. In measuring the coefficient of viscosity it is necessary that the apparatus can be easily cleaned, that the required quantities can be accurately measured, and that the conditions can be readily reproduced.

These requirements are fulfilled by the method just described, but the advantages of measuring the coefficient of viscosity by the oscillating sphere method can only be determined by further experiments in which the force is measured when the conditions agree with those required by the theory.

ENTLADUNGSSTRAHLEN AT ATMOSPHERIC PRESSURE AND AT DIMINISHED PRESSURES.

BY ELIZABETH R. LAIRD.

THE experiments described in this paper form a continuation of some already published[1] which showed that in addition to causing thermoluminescence Entladungsstrahlen ionize the air and other gases. The object of the present experiments was to observe the effect of the radiation under varied conditions in order to determine more definitely its relation to other radiations. During their progress a paper by Wood[2] bearing on the subject appeared, which showed that a radiation from the spark produces luminosity in the gas through which it passes, and that this is diminished if oxygen is blown through the chamber, but increased with nitrogen, and that the spectrum of the luminosity shows water bands.

The experiments naturally fall into two groups, that in which the source of the radiation was the spark in a gas at atmospheric pressure, under which the effect of gases on the radiation is given, and that in which the pressure around the spark was reduced. In the first group of experiments the general experimental method and apparatus used was similar to that already described.

The capacity of the gold leaf system and connections was about 4.5 E.S. units, and a change in potential of 1 volt corresponded to a change in deflection of 1.25 scale divisions, hence an ionization leak of 1 scale-division per second corresponded to a current of 4×10^{-12} amperes.

PENETRABILITY OF VARIOUS SUBSTANCES.

One of the chief difficulties in experimenting with this radiation has been that it is so readily absorbed by solid substances, and as long as the thermoluminescent effect was used as a measure of transmission, it was difficult to make sure that any slight apparent transmission was not due to light. By using the ionization effect, with turpentine in the ionization chamber for increased sensitiveness, a number of substances have been found to transmit the radiation slightly.

In these experiments, the spark was generally 4 cm. above the window of the ionization chamber so that light, of wave-length greater than λ 1,000, which is not transmitted by quartz would be absorbed by the air. The rate of leak was observed with the metal gauze over the window, with the substance in question, and with quartz 0.6 mm. thick. The leak in this latter case was rarely more than 1 scale-division a minute and more usually less than ½ scale-division a minute. This leak would include the natural leak of the electroscope. The leak with turpentine vapor in the chamber was 50 scale-divisions in one or two seconeds. Some results are given in the following table.

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[1] PHYSICAL REVIEW, XXX., p. 293, 1910.

[2] Phil. Mag., XX., p. 707, 1910.

TABLE I.

Substance.	Weight per Cm.^{2} in Mg.	Fraction Transmitted.
Aluminium	.16	.015
Aluminium	2.8	.002
Collodion	.03	.18
2 layers collodion		.04
Collodion	.17	.02
Goldbeater's skin	1.1	.0005
Tissue paper	1.8	.10
2 layers tissue paper		.002
Paraffined paper	2.6	.009
Mica	3.0	.0001
Air	1.2	.77

Since under the best conditions there was no greater leak with quartz in place than when the chamber window was covered with thick metal, it was assumed that quartz 0.6 mm. thick does not transmit this radiation, and the leak through quartz was subtracted from all results to obtain the true ionization. In this way, any error due to the action of ultra-violet light on the walls of the chamber was corrected.

The aluminium weighing 2.8 mg. per cm.^{2} was roughly tested to find the ratio of the area occupied by holes to the total area. The fraction of light transmitted was computed as .0002, indicating a true transmission through the aluminium of small amount. The tissue paper was full of holes, but the paraffine paper would withstand moderate differences of gas pressure on its two sides for some time. The amount transmitted by thin mica was too small to be sure of. In the case of collodion films it will be observed that the thick film lets through more than would be computed on an exponential absorption law in comparison with the thin, while two separate thin films do not.

The absorption of air was measured by using spark distances, 4, 8, 12 and 16 cm., and inserting the values of the intensity of the ionization produced in a formula of the form

$$\frac{I}{I'} = \frac{r'^2}{r^2} e^{-\lambda(r'-r)}.$$

The result of one experiment is given below.

Spark Distance, Cm.	Time for Leaf to Pass Over 50 Sc. Div. in Sec.	$e^{-\lambda}$ from Consecutive Observations.
4	4	
8	43	.78
12	310	.75

The average of a number of experiments gave $e^{-\lambda} = .77$, or a layer of air 1 cm. thick absorbs 23 per cent. of the radiation.

Objection might be made to the previous results on the ground, that, when the window of the chamber is protected only with metal gauze, ions might be carried in from above. The test, described in my previous paper, of placing a second shallow ionization chamber above the window of the first, and observing the leak in the lower chamber with the electrode of the upper charged and not charged, was repeated a number of times under greatly varied circumstances. Since the leak in the lower chamber was unaffected by conditions in the upper, and since with the upper electrode charged a saturation current was obtained in that chamber, the former conclusion, that in all cases the ionization observed is produced in the lower chamber, was amply confirmed.

PENETRABILITY UNDER VARYING CONDITIONS.

The experiment was tried of measuring the fraction transmitted by collodion films at different distances from the spark, as in passing through the air some change might take place in the radiation. The changes noted were too slight to be considered. Experiments were also made to compare the fraction transmitted by films when capacity was used parallel to the spark and when not. While variations were observed, it was found impossible to confirm results on different days. Where differences were observed the fraction transmitted when the source was the spark without capacity was less.

During the experiments on the transmission by films an interesting effect of the turpentine vapor was observed, which probably caused some of the irregularities, namely, it was found that the fraction transmitted by the film as estimated by the ionization in the chamber depends on the amount of turpentine vapor present. Results on a film which was kept over five weeks are as follows:

To show that this result is not due to the presence of an absorbing layer of turpentine vapor in the air above the ionization chamber, or to a radiation given off by the films themselves which is capable of ionizing turpentine vapor, the spark was placed 7 cm. above the window

Fraction of Radiation Transmitted.

Date.	Turpentine in Chamber.	No Turpentine in Chamber.
Oct. 27	.16	
Nov. 3	.16	
Nov. 10	.14	.04
Nov. 17	.15	.02
Dec. 1	.15	.048

of the ionization chamber, and a film placed directly over the window, and at heights 1, 3, 4 and 5 cm. above it. The rate of leak in the ionization chamber was found to be independent of the position of the film.

Another interesting phenomenon showed itself in these experiments, namely, that the increase in the rate of leak due to the presence of turpentine vapor is much greater when the source is the spark without capacity than when capacity is used. The introduction of turpentine vapor into the chamber, when the source of radiation was the secondary spark from the Leyden jars, increased the leak between 30 and 40 times, whereas the introduction of the vapor in the other case increased it about 100 times; or whereas the effect observed with the discharge from the Leyden jars was about 12 times as great as with the form of spark used without jars, when turpentine was admitted it was only five times as much. The value of this latter ratio taken at long intervals varied only from 4.6 to 6, but the former ratio varied considerably, owing probably to some contamination of the air.

Effect of the Walls of the Ionization Chamber.

According to Bragg, radiation of the γ ray type does not ionize a gas directly, but the ionization is produced by secondary radiation from the walls of the chamber or from the gas itself.

In the case of this radiation, the absorption is such that one would not expect much effect from the walls of the chamber, and the dimensions are such that it was usually only the bottom on which the radiation would fall. As a test, the corroded brass bottom was changed for a lead one; the average time taken to pass over 50 scale-divisions with brass was 17.9 sec., with lead 16.9 sec. Once it was found very difficult to restore the chamber to its normal state after it had had turpentine in it a long time, and in order to see if this might be due to a layer of something over the surface, aluminium was put on the bottom of the chamber. The leak was slightly diminished but not sufficiently to show anything but that the aluminium covered over one of the surfaces which supplied vapor to the chamber. The removal of the metal gauze covering the window, in conditions where the gold-leaf remained steady, increased the rate of leak in a proportion that might be expected from the increased area of the opening. These various experiments indicate that the main effect must be in the air itself.

Effect of Gases on the Production of the Radiation, their Absorption, and the Ionization in Them.

Several methods have been used for observing the effect of gases on this radiation, and distinguishing between their action on its production and transmission. Fig. 1 shows a spark chamber and ionization chamber combined, in which the upper part was glass put on with sealing wax. The whole was made tight so as to stand a diminution of pressure to about 5 cm. of mercury. A stream of gas was passed in at the lower inlet and out at the upper. Three effects are superposed here. The lower part was also used separately, with its window covered with paraffined paper, to determine the ionization produced in different gases by the emission from a source in air. A spark tube, as indicated in Fig. 2, was used to examine the effect on the production and absorption of the emission. This tube had three electrodes, one of which, *B*, could be moved to the dotted position. In this way the spark gap could be placed 2 mm. or 1.2 cm. above the opening *A*. The electrodes were put in with sealing wax, and the window *A* was covered with paraffined paper melted on. Observations were made while a slow current of the gas was flowing through, and were compared with those obtained with an air current under like conditions.

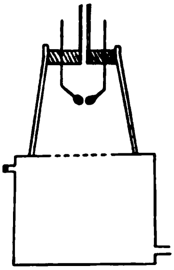

Fig. 1.

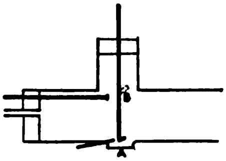

Fig. 2.

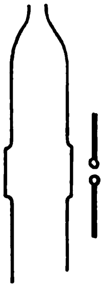

Fig. 3.

In the case of carbon dioxide, and oxygen, the absorption was also compared directly with that of air by passing a current of the gas through a tube which contained two windows covered with thin collodion films as shown in Fig. 3. The space between the windows was 2.2 cm. The tube was so placed that the radiation from the spark passed through the windows and gas in question, into the ionization chamber.

(*a*) *Hydrogen.*—With hydrogen filling the apparatus of Fig. 1, the rate of leak was too small to be measurable (0 sc. div. in 50 sec.). When, however, the apparatus had been pumped out four times, and air let in, the ionization leak was 50-scale-divisions in 1 second, and it was found difficult to restore normal conditions. The electrodes were then allowed to lie in an atmosphere of hydrogen, the result was the same as that obtained before they had been so treated. On the other hand when about ½ c.c. of hydrogen was introduced into the ionization chamber, the leak increased forty times. This seemed to make clear that the effect of hydrogen in small amounts was not to change the emission, but the ionization produced by it.

It might be thought however that this effect needed the presence of ozygen as well as hydrogen, and a number of attempts were made to try hydrogen alone in the ionization chamber. After trying thin aluminium and thick collodion films over the window of the chamber, placed window down, I finally used paraffined paper as stated above, and kept a slow air current blowing above the top of it during the experiments. Hydrogen, generated in a Kipp in the ordinary way, was passed through a wash-bottle of potassium permanganate, and then through a long drying-tube of phosphorus pentoxide, and so into the chamber and out to a small burner which was kept lighted. The result was that the ionization leak obtained was twelve times that obtained with air and such traces of hydrogen as remained from having used it repeatedly in the chamber. This should be multiplied about four times for comparison with normal air. From the results given below on the absorption of hydrogen it will be seen that any slight amount of hydrogen in the air above the window would appreciably diminish the intensity of the radiation entering the chamber, so that probably the value obtained is too low. Also, since the radiation must be absorbed rather close to the window, the result is not a comparison of the ionization produced in equal volumes of the gases.

With the apparatus of Fig. 2, hydrogen prepared as above, also prepared electrolytically and passed through two drying tubes with glass connecting pieces, was used. In the lower position of the spark the ratio of the ionization obtained to that with a similar current of dry air was .57; in the upper position approximately .02.

Supposing this difference due to an absorption of 1 cm. of hydrogen, knowing that for air, one computes that 1 cm. of hydrogen absorbs 97 per cent. of the emission, and that two millimeters would transmit 49 per cent. This would agree well with the supposition that the emission from the spark in hydrogen is approximately the same as that from the spark in air, since when each of the radiations had 2 mm. to travel in the respective gases the proportion emerging in the case of hydrogen was 57 per cent.

These results are so different to those of Hoffmann, who found the thermoluminescence in hydrogen very bright, that one finds it easy to conclude that in the case of hydrogen his effects were due to ultra-violet light.

With oxygen in the chamber of Fig. 1, the ratio of the ionization observed to that with air was from one fourth to one sixth. With a current of oxygen from a cylinder, flowing through phosphorus pentoxide and glass wool into the ionization chamber, an ionization 1.6 times that produced in air was observed. With the apparatus of Fig. 2 and the lower position of the spark, the radiation observed was three fourths that with air; when the upper electrodes were used the ratio was only one fifth. This makes $e^{-\lambda}$ for oxygen .20 and the fraction transmitted by 2 mm. of the gas .73. This agrees well with the supposition that the emission of the radiation is the same in oxygen as in air and that the diminution noted in the upper position of the electrodes was caused by absorption.

This large value for the absorption of oxygen does not agree however with the value of the ionization obtained when both spark and ionization chambers were filled with the gas, nor with the results of the writer showing no great absorption by oxygen as tested by the thermoluminescent method. An explanation of the discrepancy may be given, namely, that the layers of oxygen in a confined space close to the spark absorb more strongly than those at a distance in a more open space; and this suggestion receives some confirmation in the following observations. It was noted at various times that when air was blown between the spark and the ionization chamber the ionization in the chamber increased slightly. During the experiments in which the spark was in a tube as described above, slight changes in the leak were noted depending on whether there was a current of air flowing through or not. When the electrodes were in the upper position this difference was very marked, as when the ionization leak changed from 50 scale-divisions in 13 sec. to 50 in 32 sec. when the air current was stopped. These observations indicate that changes in the gas produced under the action of the spark increase its absorption, and that the effect is further increased when the gas is in a closed tube when such products might accumulate. For this reason in using such a tube air was kept flowing through when the air comparison was made. The same was true of the other gases, but it is quite possible that with oxygen the effect was greater than could be avoided in this manner. The absorption of oxygen was therefore examined by the method illustrated in Fig. 3. No difference was detected between the case when air was flowing through the tube and, when oxygen was flowing. From this one would conclude that at a distance from the spark, oxygen has the same absorption coefficient as air.

(*c*) *Nitrogen.*—Nitrogen was prepared from potassium nitrite, ammonium chloride, and potassium bichromate, collected over distilled water, and passed through two drying tubes and a plug of glass wool into the spark tube of Fig. 2. The ratios of the ionization produced, to that with air in the tube, were respectively .85 and .77 for the lower and upper positions of the electrodes. From this $\epsilon^{-\lambda}$ for nitrogen is .7 and a thickness of 2 mm. of the gas would transmit .93 of the radiation falling on it. This is not very different from the amount observed, on the supposition that the radiation in nitrogen is the same as in air.

Nitrogen prepared by passing air slowly over red hot copper through a strong solution of caustic potash, drying tubes, and glass wool, was passed through the ionization chamber. The rate of leak was 6 times that with air. This being unexpectedly large, it was strongly suspected that some vapor had been carried over with the nitrogen. Later, with the apparatus rearranged so that the air passed first through the caustic potash and drying tubes, and then over the copper, an ionization between .7 and .8 that in air was obtained. It seemed possible that in the first case some trace of hydrogen, or hydrogen compound, had been carried over.

(*d*) *Carbon Dioxide.*—Experiments with the apparatus of Fig. 1 gave an ionization from one sixth to one tenth that in air. With the gas in the ionization chamber only, the ionization was .6 that in air. Using the method of Fig. 3 to determine the absorption produced by carbon dioxide, it was found that the rate of leak with the gas in the tube, to that with air flowing through was .19. This gives for carbon dioxide $\epsilon^{-\lambda} = .36$, or indicates an absorption by 1 cm. of the gas of 64 per cent.

Applying this value of the absorption to the first result it would appear that the radiation is emitted quite as much in carbon dioxide as in air; but using the spark tube of Fig. 2 in a long series of experiments, a radiation of about .1 that in air was observed in the lower position of the electrodes, and of .04 in the upper position. These values agree relatively with the experiments on absorption, but the small ratio in the lower position could not be explained by an absorption of 2 mm. of the gas. It was noted that whenever carbon dioxide was introduced into the spark tube, the spark had more difficulty in passing. It is clear also that if the tube leaked around the window the absorbing layer would be thicker than that assumed. Hence further experiments were made with the spark tube placed window up below the ionization chamber. In these the primary spark of the induction coil was used, and in some a small spark gap, in series with the main one, was placed between a point and a revolving drum so that one was enabled to count the number of sparks. The gas current was made slower, also, as the stronger current seemed to blow out the spark. The average of these experiments gave the ratio of the radiation in carbon dioxide to that in air .34, or allowing for 2 mm. absorption .4. As this was the only gas in which the emission of the radiation seemed noticeably different to that in air, the first experiments were repeated with the apparatus of Fig. 1. The electrodes, which were small steel balls, were used at heights 2 cm. and 5.5 cm. above the ionization chamber. From the results at the two heights the fraction transmitted by a layer of 1 cm. of carbon dioxide was computed as .39, in fair agreement with the .36 obtained earlier, and the fraction .80 was found for air. But at the height 2 cm. the ratio of the effect with carbon dioxide to that with air was .26, and, allowing for the absorption, this would mean an emission in carbon dioxide equal to that in air, or greater if one takes into account the fact, that not as great an ionization is produced in carbon dioxide as in air by the same radiation. That this result with the closed chamber was not due to a direct diffusion of ions from the spark into the chamber, is shown by the fact that in the similar case of hydrogen no leak was obtained. The carbon dioxide used in these experiments was obtained from a cylinder containing the liquid, and was passed through drying tubes and glass wool, sometimes the drying tubes were omitted. Whatever impurities were present in it, would be present in all cases, and would not account for the variety of results. It is to be noted that in using the spark tube the radiation had to pass through paraffined paper, and it is possible that the penetrability of this radiation differs from that produced in air, or that the radiation from the spark in carbon dioxide produces relatively more ionization in carbon dioxide than radiation from a source in air. It is to be remembered also, that the electrical conditions in the experiments with carbon dioxide are necessarily different from those in air. In the latter experiments the spark balls had to be placed closer together in carbon dioxide than in air to make the induction coil function properly.

(*e*) *Turpentine Vapor.*—It seemed worth while to test whether the large increase in the ionization in the presence of turpentine vapor depended on the gas in the chamber. Hydrogen, carbon dioxide and air were in turn caused to bubble through turpentine, and were passed into the ionization chamber, with the window covered with paraffined paper as before. In each case the ionization was greater than with the gas alone. The results were as follows:

Hydrogen + turpentine vapor 50 sc. div. in 25 sec.
Carbon dioxide + turpentine vapor 50 sc. div. in 78 sec.
Air + turpentine vapor 50 sc. div. in 35 sec.

(*f*) *Chlorine.*—Chlorine was tried in the ionization chamber, but without definite result as the insulation rapidly deteriorated. It was observed, however, that a small amount of chlorine increased the ionization.

Table II. gives an oversight of the main results with gases. I believe that relatively it indicates the facts, although on account of the difficulties in avoiding impurities, where the gases come in contact with metal, no great accuracy can be claimed for the figures given.

TABLE II.

Gas.	Emission Compared with Air.	Ionization in.	Fraction Absorbed by 1 Cm.
Air	1	1	.23
Oxygen	1+	1.6	.23
Oxygen near spark			.80
Nitrogen	1−	.7	.3
Carbon dioxide	.4 in tube 1 outside	.6	.64
Hydrogen	1+	50	.97

Since it seems possible that the luminosity photographed by Wood is due to the ionization of the gas by the Entladungsstrahlen, it is interesting to observe that these results offer a partial explanation of his. Since the presence of oxygen close to the spark, in an enclosed chamber, greatly increases the absorption, diminished luminosity at a given distance would result, while a strong current of nitrogen would diminish the amount of absorbing vapors present; also the fact that traces of hydrogen increase the ionization greatly, may possibly account for the spectrum obtained by him.

RADIATION FROM THE DISCHARGE IN AIR AT LOWER PRESSURES.

In beginning the second group of experiments the spark tube of Fig. 2 was used, in which the pressure could be reduced to about 40 cm. of mercury. Down to this pressure the radiation showed no change. It was found unsatisfactory to use more heavily paraffined paper over the window at lower pressures, as the penetrability of the paper varied during the experiment. After one experiment had shown a perceptible increase in the ionization at a pressure of about 2 cm. of mercury, aluminium was used to cover the window, and tubes of the forms I., II. and III. in Fig. 4 were used. The window was 3 or 4 mm. in diameter, and the spark gap was from 5 mm. to 1.2 cm. above it. The tubes were connected to a pressure gauge on the one side and to the pump on the other. The pressure was lowered to about 2 mm. of mercury with a Geryk oil pump, and later to lower pressures with a mercury pump. The accompanying curve, *A*, Fig. 5, shows the result of a series of consecutive observations at pressures varying from 4 mm. to 30 mm. The curve *B* is the same but with the ordinates enlarged ten times. The rapid rise in the ionization produced as the pressure is diminished, is at once remarked. This rise in the curve continues as the pressure is further diminished, the ionization being eight times as great at a pressure estimated as one half a millimeter, as at five millimeters.

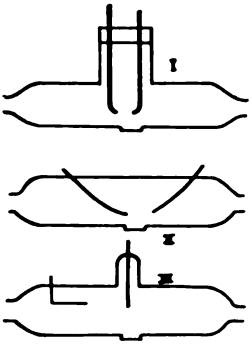

Fig. 4.

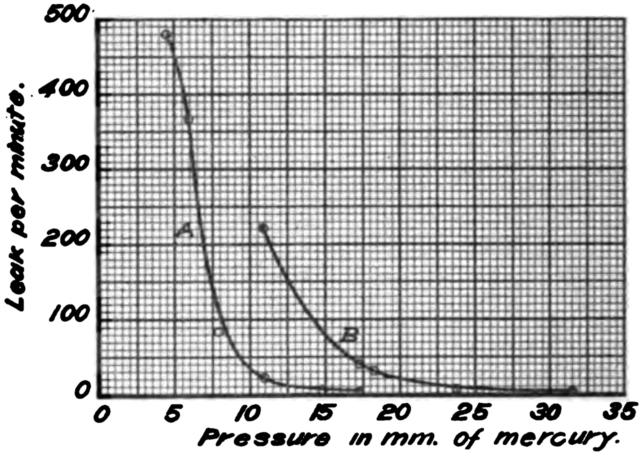

Fig. 5.

PENETRABILITY OF THE RADIATION AT LOW PRESSURES.

The fraction of this radiation transmitted by thin layers of various substances is much greater than when the source of radiation is the spark at atmospheric pressure, but quartz in a thickness of 0.6 mm. is opaque as before. For example, when the ionization rate of leak was 3 scale-divisions per second, no leak was observed through a quartz plate in 30 seconds. Results obtained with three other substances and compared with those for the spark at atmospheric pressure, are as follows.

	Fraction Transmitted at Atmospheric Pressure.	Fraction Transmitted. at a Pressure of 6 mm.
Collodion film	.009	.5
Paraffined paper	.006	.5
Aluminium foil	.003	.35

To examine the absorption in the case of air, the spark tube was placed at heights .9 cm., 1.9 cm., 2.9 cm., and 5.3 cm. above the ionization chamber. As it was estimated from the relative size of the openings in the ionization chamber and in the spark tube, that the emergent beam if coming from the spark would approximately all enter the ionization chamber at the greater height, the simple formula $I = I_0e^{-\lambda x}$ was used for the computation of λ. The average value was found to be .67. This is somewhat low, as the variation of intensity with distance alone would not be entirely negligible, and it seems probable that the value of the absorption coefficient for this radiation is about the same as for that at atmospheric pressure. Results with mica and cardboard are given in Table III.

The values of the transmission by aluminium and other solid substances being unexpectedly large, tests were made to see if this change in penetrability was gradual. Down to 20 cm. pressure no change in the penetrability of the radiation was indicated. At the pressure where the ionization first begins to increase, the total amount, when the aluminium window was used, was too small to make determinations of absorption feasible. At lower pressures, strong indications of gradually increasing penetrability appeared, as is shown in Table III.

TABLE III.

	Fraction of Radiation Transmitted.					λ	λ/d
	15 mm. of Hg.	9 mm. of Hg.	6 mm. of Hg.	3 mm. of Hg.	.5 mm.? of Hg.		
Paraffined paper	.25	.43	.5				240
Aluminium .0011 cm. thick	.31	.32	.35	.53	.63	580	230
Cardboard .025 cm. thick		.17		.32	.38	45	45
Cardboard .05 cm. thick				.12		42	
Mica .0021 cm. thick		.18		.40	.48	440	170
Mica .0065 cm. thick				.12		320	130
Air 1 cm				.77?		.27	225

As the pressure-ionization curve is steep, changes take place in the ionization observed when there is no noticeable change in the pressure as measured by a common mercury gauge. But by rapidly alternating observations with and without the absorbing layer, reliable results could be obtained. The observations with the aluminium, the cardboard, and the thin mica were repeated a number of times.

In the last two columns of Table III. are given the values of the coefficient of absorption of the substances for a pressure of 3 mm. except for the paper where it is given for a pressure of 5 mm. They are derived from the equation $I = I_0e^{-\lambda x}$, where I is the observed rate of leak with the absorbing layer, I_0 that without, and x the thickness. The ratio of this coefficient to the density is also given, the quantity xd being found by weighing.

Considering that the absorption varies with the pressure in the discharge tube, a relation between it and the density could not be expected. The fact that this ratio is about of the same order, cardboard showing the greatest deviation, indicates little selective transmission.

SOURCE OF THE RADIATION.

That this radiation proceeds mainly from the neighborhood of the cathode is easily seen by changing the direction of the discharge. The greater value was always obtained with the cathode over the window. The ratio of the effects observed with cathode and anode in this position was one time as great as 25 to 1. This might lead one to think it possible that in a strictly unidirectional current the whole of the penetrating effect would come from the cathode.

The field of a small electromagnet, quite powerful enough to strongly deflect ordinary cathode rays, produced no effect on the radiation. The same was true when a large electromagnet was used unless the discharge tube was close to the poles. In this case the radiation entering the ionization chamber was diminished in amount, and more so, to about one third normal, when the spark tube was placed between the poles.

This was evidently not a direct action on the radiation. Probably it was due to the action of the magnetic field on the form of the discharge. An experiment was made, however, to test whether the radiation was due to the impact of weak cathode rays on the aluminium window, as such rays would be deflected by a magnet. For this purpose a tube as indicated in Fig. 6 was used. *MM* denote the poles of the magnet and *A* the aluminium window. In these circumstances the radiation was not at all affected in amount by the magnetic field. Experiments were also made in which the opening in the spark tube was covered with mica. The radiation was obtained as before. These various observations point to the conclusion that the source of the radiation is the discharge in the neighborhood of the cathode.

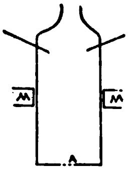

Fig. 6.

EFFECT OF TURPENTINE VAPOR, OF HYDROGEN, AND OF THE WALLS OF THE VESSEL ON THE IONIZATION.

This radiation differs markedly from that at atmospheric pressure in the absence of any particular effect of turpentine vapor on the ionization produced by it. At a pressure of 20 cm. of mercury the effect noted at atmospheric pressure persists. In some early experiments a slight increase in the ionization with the introduction of turpentine appeared at the lower pressures used, but with better arrangements whereby the bottom of the ionization chamber could be moved without disturbing the rest of the apparatus, no effect was obtained at a pressure of 3 mm., and the addition of some hydrogen to the air in the chamber diminished the rate of leak.

To test the effect of the walls of the vessel, an ionization chamber of depth 4 cm., and dimensions such that the radiation from the spark tube placed immediately above the window would not reach the sides of the vessel, was used with different bottoms. The rate of leak with black paper, aluminium, lead and brass was the same. Thus it would appear probable that secondary radiations from the walls of the vessel do not cause any large portion of the ionization.

DISCUSSION OF RESULTS.

Considering first the radiation from the spark at atmospheric pressure, I have already pointed out, in the paper referred to earlier, that this radiation is not of the α or β type, nor light of wave-length greater than λ 1,000; and the facts covering penetrability given here amply bear this out. The earlier investigations showed that the radiation travels rectilinearly, casts sharp shadows, is not deflected in a magnetic field, is not altered by a change of the materials of the electrodes, is very slightly reflected from materials such as glass, paper, copper, lead.

Comparing its properties with those that might be expected of light of extremely short wave-length, it is evident that this radiation is not of a definite wave-length, since varying the capacity varies the relative effects produced on air and on turpentine vapor, and also varies its transmission by thin collodion films. The penetrating qualities are remarkable for light. Hydrogen is transparent to the extreme ultra-violet as far as known, and is very opaque to this, while air is relatively transparent, and aluminium, paraffine, and paper are somewhat so. One realizes, however, that one cannot predict with certainty the behavior of substances with respect to unknown light, and it might be said that the absorption of hydrogen shows a selective quality most easily explained in this way. The ionizing properties are in line with what is known concerning the effects of ultra-violet light, since these increase with diminishing wave-length and are greater with vapors of high molecular weight. Hydrogen, however, as shown by Palmer[1] is ionized very little by light of the shortest known wave-length. Further evidence that this is not light of definite wave-length is found in the fact that changes in the material of the electrodes, and in the gas in which the discharge takes place (except in the case of carbon dioxide), do not change appreciably the amount of the radiation. The difference in the case of carbon dioxide may be more easily ascribed to changed electrical conditions than the sameness in the other cases to identical light conditions.

On the other hand the properties possessed by this radiation are approximately those to be expected of the radiation of Röntgen ray type, which, according to Sir J. J. Thomson's theory of the spark discharge, is always present, due to the accelerated motion of electrons. This would differ from light of short wave-length in the lack of definite periodicity. Hydrogen shows even for penetrating Röntgen rays abnormally high absorption and ionization values. Also for the less penetrating rays the absorption is not proportional to the mass traversed. Thus radiation from the spark at atmospheric pressure might be inferred to have penetrating and ionizing qualities such as the Entladungsstrahlen possess. The approximate sameness of the radiation with different electrodes and in different gases would then be explained, as also the change in character with the addition of capacity, and the non-homogeneity of the radiation.

Turning to a consideration of the rays from the source at low pressures, one sees that they also are not of the β ray type, since not deflected in a magnetic field, nor of the α ray type, since they are more penetrating than these, nor light of wave-length greater than λ 1,000 since air transmits them and quartz cuts them off.

This radiation, also, is not light of definite wave-length since it increases in penetration as the pressure is diminished, and the absence of marked selective absorption as well, points to a radiation of the Röntgen ray type. It does not appear to me that a radiation of the neutral doublet type as described by Bragg, could have the varied penetrating qualities of these radiations nor is there reason to expect here a radiation of this type.

The question may be raised whether the two radiations are of the same nature, since the penetrating qualities are so different. In favor of this is the fact that the ionization is continuous in amount, and, that, while experiments have not yet been devised to measure the penetrating qualities at the transition stage, the penetrability has been shown to increase gradually at lower pressures. Investigation may show however an abrupt transition, since the radiation from the spark at atmospheric pressure comes from the whole length of the spark and is only a fraction greater from the cathode, whereas at low pressures the penetrating part is almost entirely from the neighborhood of the cathode. Radiation from electrons in this region might be always more penetrating than from the electrons along the path of the discharge.

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[1] Physical Review, XXXII., p. 1, 1911.

In conclusion, then, while a number of points remain to be investigated, it may be said that the experiments described here help to confirm the general theory of Sir J. J. Thomson concerning the spark discharge, and to show that the Entladungsstrahlen are an electromagnetic radiation with properties approaching those of light, differing from light in lack of definite periodicity, and becoming more penetrating at lower pressures. They show also that the ionization caused by this radiation is large in amount so that it must play quite a part in the passage of the discharge.

Note.—The writer has just seen in the Revue Scientifique of April 29, 1911, a report on some work done by Lenard and Ramsauer, in which they used the spark from a powerful transformer with a large battery of condensers, and obtained effects which in some respects resemble those given above, notably in the action of vapors, but which differ in the large value of the ionization obtained in carbon dioxide, and more important, in that their radiation was transmitted both through air, and through several millimeters of quartz, and through fluorite. For this reason the authors infer the effect to be due to light of wave-length less than 1,000 Ångström units. The account given does not tell how the authors distinguished between these new effects and the effects of the "Entladungsstrahlen" which must have been there when quartz was not used, and those of ultra-violet light from the Schumann region which, with such a powerful source, must surely have been present when quartz was used.

July, 1911.

NOTE ON ELECTRICALLY PRODUCED WATER RIPPLES.

By Frederic Palmer, Jr.

A SIMPLE method of producing water ripples by means of the discharge from an induction coil was first devised by H. Schultze,[1] and utilized by him as a frequency meter. More recently Pfund[2] has called attention to the value of ripples produced in this way as an aid to the study of optical phenomena, and he was able to photograph some interesting cases of interference and diffraction. He points out that the advantage of this method of ripple production lies in its simplicity and ease of manipulation. In the way of making the mechanism of interference and diffraction phenomena clear, unmistakable, and vital to students, however, the method, as described by Pfund, is slightly lacking in some particulars; for only one or two persons can see the phenomenon at the same time, moreover the source of illumination is very weak, and the ripples are very small.

I have found that it is easy to modify this experiment so that none of the above objections apply. The current from a 110-volt A.C. lighting circuit is sent through the primary of a six-inch induction coil (*I*, Fig. 1), the ninety-degree arc (*A*) in a Bausch and Lomb Universal Balopticon arranged for vertical projection, and a variable resistance (*R*), all in series. From the secondary (*S*) of the induction coil wires are carried to distilled water in a thin flat-bottomed evaporating dish (*D*), placed on the vertical condensing lens (*C*). A variable resistance (*r*), shunted about the induction coil, permits of change in the intensity of the discharge from the secondary terminals (*T*) while at the same time producing little change in the main current through the arc. The variable resistance (*R*) should be so adjusted as to permit the passage of only a small current, barely

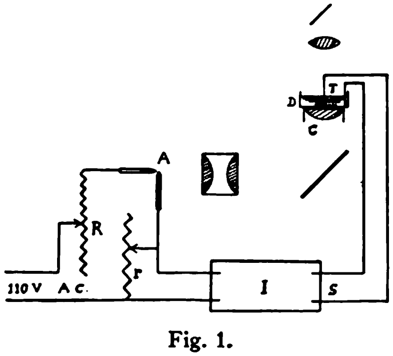

Fig. 1.

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[1] Zeitsch. für Instrumen., p. 150, 1906.

[2] Phys. Rev., March, 1911, p. 324.

enough to keep the arc going well. This makes the arc as small as possible, and thus sharpens the image of the ripples on the screen. Extra small, pointed, carbons should be used. If one of the secondary terminals (*T*) is placed deep in distilled water in the carefully cleaned evaporating dish, near its edge, while the other is allowed just to touch the water surface near the center, excitation of the arc produces sharply defined circles on the screen, which can be seen simultaneously by a large number of persons. Upon bringing out the other secondary terminal to the center of the dish, and raising it till it also just touches the water surface, interference fringes appear; and it is most interesting and instructive to the student to watch the number, the sharpness, and the curvature of the hyperbolic sheets change as the two sources of disturbance are moved nearer together or farther apart. As terminals dipping into the water, I have used platinum wires about .5 mm. in diameter. These may be given a sharp point, while they do not fuse in case the terminals come out of water entirely, as small copper wires or needles do.

Evidently all the experiments described by Pfund may be shown with the apparatus arranged as above, with the added advantage that a number of observers are enabled to see the phenomena taking place at the same time. Moreover the illumination is strong, and the ripples appear on the screen large and circular instead of elliptical. The experiment on ripple refraction through an oil drop, which Pfund was unable to photograph, can be seen taking place by all at once.

Observations of secondary interest are connected with the luminosity of the arc, and with surface tension. Since the current through the arc changes direction sixty times a second (60 cycles), it is of interest to note that the difference in luminosity between the horizontal carbon, when cathode and when anode, is sufficient to produce the intermittent illumination desired. This was found to persist as the current through the arc was increased up to twenty-five amperes. That this change in luminosity actually takes place is easily shown by placing the arc in a separate circuit from the induction coil, and running it, as ordinarily, with a direct current. The circles surrounding the points of disturbance disappear at once; while interference fringes may still be seen for a short distance only between the two sources. When the current through *I* is too large a thin stream of water[1] is sometimes drawn three or four centimeters up one of the secondary terminals (*T*), where it plays up and down like a miniature fountain, producing, however, disturbing effects upon the ripple phenomena. This may be regulated by the variable shunt resistance (*r*). The ripple phenomena are best produced with cold distilled water. As this becomes warm the change of surface tension is easily noticeable; moreover, curved lines resembling lines of flow appear, extending from one point source to the other.

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[1] H. Schultze, Zeitsch. für Instrumen., p. 151, 1907.

Haverford College,
July, 1911.

THE THERMOELECTRIC BEHAVIOR OF HEUSLER ALLOYS IN A MAGNETIC FIELD.

By L. O. Grondahl and S. Karrer.

THE effect of a magnetic field on thermoelectric behavior has been studied by a number of experimenters and with a variety of results. The lack of agreement and of complete data on the subject led the authors to prepare for some experiments on the effect of direction, magnitude, and the nature of the field. The statement by Guthe and Austin[1] that they had looked for the effect in Heusler alloys and that there was none found as great as .5 microvolt, together with the interesting theoretical bearing attributed to it, made it seem worth while to look for the effect with a more sensitive arrangement of apparatus. So the other experiments were postponed and the present report deals almost entirely with the work on the alloys, the results of which seem sufficiently interesting to warrant publication at this time. Investigation of the other points mentioned will be continued.

The method adopted is the same as that employed by Guthe and Austin.[2] As shown by the diagram, Fig. 1, the greater part of the E.M.F. of the couple is balanced by means of a storage cell and a potentiometer. The galvanometer is a low resistance Broca, the sensibility varying around 5×10^{-7} volts per cm., the scale being at a constant distance of about 2.25 meters. R_1 and R_2 are Leeds and Northrop decade boxes. The field current was varied by means of a lamp bank rheostat. The coil used in the preliminary experiments gave a maximum field of about 400 gauss. For the later experiments another coil was built for which the constant at the center was calculated at 114.7. It was 35 cm. long, 4 cm. internal diameter, and 20 cm. external diameter. It was built of No. 9 copper wire and had a short time capacity of about 25 amperes, giving a maximum field of about 2,800 gauss. Calculation gave for the

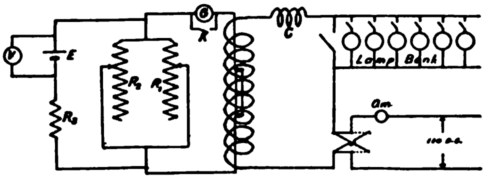

Fig. 1.

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[1] B. of S. Bul., Vol. II., No. 2, p. 315, 1906.

[2] Loc. cit.

field at 5 cm. away from the center on the axis, $H = 114.1I$, showing a fairly uniform field for at least 10 cm. along the axis. Theresults with the two coils were found to agree throughout. The field coil was placed about 10 meters away from the galvanometer and its field at the galvanometer was neutralized by means of another solenoid, C, in series with it, and placed near the galvanometer. The effect of the field coil was by this means neutralized so that for no current did it give a deflection greater than .5 mm. on the scale. The galvanometer and all the leads were carefully insulated to avoid grounds or leaks from the field current. K is a key used for short-circuiting the galvanometer to prevent large inductive throws while opening or closing the field circuit.

The junctions of the couple were kept, one in steam and one in circulating ice water, as indicated in Fig. 2. The water was kept moving through about 15 feet of lead pipe imbedded in cracked ice. A propeller driven by a small motor and fitted into a part of the water circuit, served as pump. The temperature constancy obtained by this means is indicated by the constancy of the zero reading as given under "zero" in Table II. The greatest variation for the whole run is 2.2 cm., corresponding to a temperature variation of .2° C. During one reading the temperature was usually constant to a few hundredths of a degree. A layer of asbestos and paper wound on the glass tube served as electrical and heat insulation.

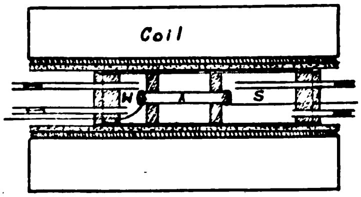

Fig. 2.

The arrangement of electrical apparatus is in principle the same as the deflection potentiometer described by Brooks.[1] A calculation similar to his shows that the galvanometer current is proportional to the difference between the two E.M.F.'s and inversely proportional to the total resistance of the galvanometer circuit. Since the latter is practically constant during an experiment, the sensibility in volts per centimeter deflection was obtained by slightly varying either R_1 or R_2, the E.M.F. of the couple being kept constant. Then

$$S = \frac{E}{d}\left(\frac{R}{R_3 + R} - \frac{R'}{R_3 + R'}\right),$$

where d is the deflection in centimeters caused by the change in R; E, the E.M.F. of the storage cell; R and R', the values of $\frac{R_1R_2}{R_1 + R_2}$ before and after the change; R_3, a constant resistance of 10,000 ohms. Experiment showed the sensibility to be practically constant over the whole scale and the effect could therefore be read in scale divisions.

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[1] B. of S. Bul., Vol. II., No. 2, p. 225, 1906.

The temperature of the coil rose to some extent during an experiment. The constancy of the zero and the fact that a Cu-Zn couple and a Cu-Al couple showed no effect whatever, seemed sufficient proof that the change in temperature of the coil had no appreciable effect on the couple. A Pt-PtIr couple placed in the same position in steam also showed no effect of the change in temperature of the coil. The effect of permanent magnetism, if present in the alloys, is thought to be negligible as far as these experiments are concerned. In the case of all the couples tested, al least two runs were made immediately following one another, and with the field in opposite directions, yet no consistent difference was found even in the small readings, although in the experiments performed no attempt was made to demagnetize between readings. In the Fe-Cu couples it was found necessary to demagnetize partly in order to duplicate the readings with low values of the field. An attempt will be made to investigate the effect of permanent magnetism further.

For the specimens of Heusler alloys we are indebted to Professor A. A. Knowlton, of the University of Utah, who kindly lent us some of the rods prepared by him in 1908 and which he described in the REVIEW.[1] In what follows, the alloys are numbered the same as there. Table I. gives the chemical composition, density, magnetic property, total E.M.F., and range of transformation, for all of which, except the column under E.M.F., we are also indebted to Knowlton. All the alloys show a trace of iron.

A bar of electrolytic iron from Professor C. F. Burgess, University of Wisconsin, a bar each of "purest" nickel and cobalt from Dr. Schuckardt, of Görlitz, and a bar of pure nickel from Kahlbaum, were kindly

TABLE I.

Specimen.	Cu	Mn	Al	Si	Density.	Magnetic Property.	E.M.F.	Transformation Range.
2	67.2	22.5	10.0	.25	6.77	Good.	.00087	225°–275° C.
3	64.9	22.0	12.6	.49	6.83	"	.00075	"
5	65.0	25.8	8.8	.40	6.86	"	.00076	"
8	56.4	29.6	13.1	.89	6.94	Poor.	.00077	"
11	70.4	19.0	9.4	1.22	7.13	"	.000367	40°–120° C.
13	72.6	20.1	7.05	.23	7.16	Medium.	.000383	"
14	72.2	17.4	10.3	.08	7.17	Poor.	.000234	10°– 30° C.

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[1] PHYS. REV., Vol. XXXII., p. 54, 1911.

placed at our disposal by Professor Osborn. The aluminium was a commercial sample and the zinc was an "arsenic-free" specimen from Eberbach & Son. Iron specimen No. 2 was a piece of rolled steel picked up in the laboratory.

The samples were all 10 cm. or less in length, and all but the electrolytic iron were .5 cm. or less in diameter. The iron bar was 1.2 cm. in

TABLE II.

Alloy No. 3.

Curr.	Zero.	Reading.	Defl.	*E*	*H*	*E*	*H*
.45	34.00 34.00	34.35	−.35	-23.6×10^{-8}	60	−20.2	60
.95	34.00 33.70	34.2	−.35	−23.6	120	−16.8	120
1.45	33.75 33.85	34.0	−.20	−13.5	175	−23.6	175
1.90	33.75 33.75	33.65	.10	6.74	230	−20.2	220
2.10	33.85 33.75	33.90	−.10	− 6.44	250	3.37	240
2.75	33.70 33.45	33.45	.13	8.76	327	10.1	315
3.50	33.45 33.40	32.90	.52	35.1	410	33.7	420
3.90	33.45 33.40	32.80	.62	41.8	447	70.7	670
5.90	33.30 33.10	32.20	1.00	67.4	670	74.1	865
7.80	33.10 33.10	31.50	1.60	107.8	875	124.6	1,115
9.50	33.00 33.05	31.20	1.82	122.8	1,095	158.2	1,210
11.00	33.00 33.00	30.80	2.20	148.2	1,260	189	1,350
12.10	33.00 33.10	30.60	2.45	165.0	1,380	162	1,495
13.25	33.10 33.20	30.50	2.65	178.5	1,530	192	1,570
14.15	33.60 33.60	30.65	2.95	199.0	1,630	186.5	1,670
15.05	33.65 33.90	30.65	3.13	211	1,725	183	1,725
15.55	34.00 34.30	31.00	3.15	212	1,775	186.5	1,800
16.80	34.30 34.70	31.20	3.30	220	1,930	189	1,862
23.75	34.70 35.20	30.50	4.45	300	2,730	296	2,600

diameter. The couple was made in each case by winding a piece of No. 18 copper wire around each end and soldering them to make good contact. In the case of the alloys an effort was made to raise the temperature as little as possible. Soft solder was used and heated just sufficiently to make it possible to spread it with the iron, thus getting a good steady contact without a really soldered junction.

The process of taking an observation consisted in noting the zero of the galvanometer, closing the field circuit, noting galvanometer reading, opening the field circuit and again determining the zero reading. The zero used was the mean of the two zero readings. A curve was gotten by taking a series of such observations increasing the current by steps. All the curves plotted are the averages of at least two such series taken with the field current in opposite directions. A sample set of observations is given in Table II. The fifth and sixth columns are calculated from the first four, the seventh and eighth are corresponding values obtained after the current is reversed. *E* is obtained by multiplying the sensibility of the galvanometer by the deflection. *H* is obtained from a curve between ammeter reading and field and is approximately 114.5*I*. The first column gives the uncorrected ammeter reading.

The results for the alloys are represented by the curves of Fig. 3,

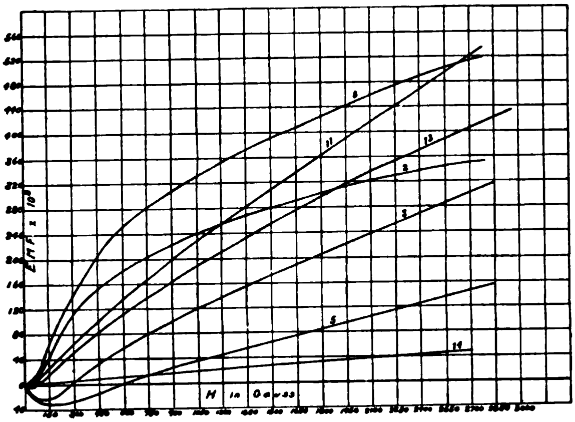

Fig. 3.

those of the magnetic metals by those of Fig. 4. The ordinates represent change in E.M.F.; the abscissæ represent the field. Positive ordinate means an increase, negative a decrease in the E.M.F. As is seen, the effect is found in all the alloys and the shape of the curves is in each case similar to that of some one of the magnetic metals. There seems to be no definite relation between the magnitude of the effect and the magnetic property of the alloys. The curves of Nos. 3 and 5 which are labeled by Knowlton "Good" in magnetic properties cross the axis, as does also that of the one labeled "Medium," No. 13. These three also seem to approach a maximum earlier than the others. Nos. 11, 13, and 14 all have low transformation points, and during the experiment, one end was probably magnetic, the other not. Whether or not, in that case, the field affected only the end at the lower temperature has not yet been determined. As seen in Table I., the E.M.F. of these alloys is about one half of that shown by those of the high transformation points, and yet the change in E.M.F. seems to approach a higher maximum in No. 11 than in any of the rest. It may be seen also, that these curves are more nearly linear than the rest. The shape of those curves which do not cross the line is very similar to that of the magnetostriction curves of Guthe and Austin.[1] One of the authors hopes to investigate the magnetostriction curves of these samples during the coming year. The magnitude of the effect in iron and nickel agrees fairly well with the results obtained by Bidwell[2] who reports a maximum of 30 × 10^{-6} for nickel and between 6 × 10^{-6} and 12 × 10^{-6} for different specimens of iron. For the Al-Cu and the Zn-Cu couples no effect is found as great as 10^{-7} volts.

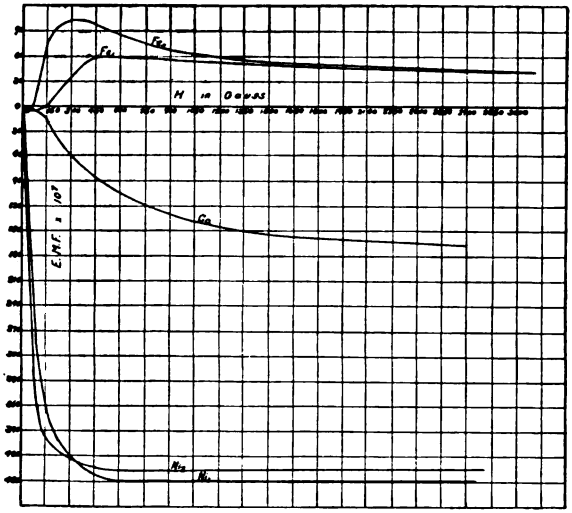

Fig. 4.

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[1] Loc. cit.

[2] Roy. Soc. Proc., 73, p. 413, June, 1904.

RESULTS.

1. The experiments show that the effect of the magnetic field on thermoelectric behavior is present in Heusler alloys, and is of the same nature as in the case of the magnetic metals.

2. The surmise that the magnetic property of the alloys is different in nature from that of iron, loses its support as far as the present phenomenon is concerned.

3. In this type of field no effect is found in the non-magnetic substances tried, aluminium and zinc. In view of Posejpal's work the effect of the nature of the field on these is to be investigated further.

4. For very low fields the effect in the case of iron samples tried is negative.

PHYSICS LABORATORY,
UNIVERSITY OF WASHINGTON,
August, 1911.

CERTAIN CHARACTERISTICS OF LIGHT-NEGATIVE SELENIUM.

BY LILAH B. CRUM.

THE change of resistance in light-positive selenium under the action of light occurs in one of two distinct types. Which is followed seems to depend in some manner upon the magnitude of the change, or, in other words, upon the sensitiveness of the unit.[1] When units of low sensitiveness, which are also of low resistance, are exposed to light, their conductivity increases rapidly at first, and then more and more slowly, while the conductivity of the high sensibility, or high resistance units rises quickly to a maximum value, and then falls off more and more slowly. But whichever type of action is followed, the selenium always shows an increase of conductivity immediately after exposure to light.

Ries[2] records the action of a selenium unit, where the fifth day after its manufacture the falling off in conductivity after the maximum had been reached was great enough to bring the conductivity in the light to a value below that which it had shown in the dark. But he concluded that this strange effect was due to the presence of moisture.

The first selenium units which decreased their conductivity immediately upon exposure to light were reported in 1910 by F. C. Brown,[3] and termed *light-negative*. Six of these units were made, all of which showed a very low resistance, five hundred to ten ohms, and one had even a less resistance. The sensibility of these units was never above fifteen or twenty per cent.

The discovery of light-negative selenium opened up two new fields of investigation: first, the problem of ascertaining the conditions necessary for the reproduction of such units at will, and second, the determination of the characteristics of those units which were already made.

The method used by Dr. Brown in the production of his light-negative selenium was somewhat as follows: He powdered the black, glassy selenium and placed it upon an ordinary porcelain insulating cleat which had been wound with a double spiral of German silver wire. Enough selenium was placed upon this cleat to give a surface of about two square centimeters. The porcelain was heated in air for perhaps half an hour and then allowed to cool to approximately 100°. It was reheated in a sand bath or oven slowly to about 210° and very slowly cooled. In each case it was taken from the oven when the temperature was not lower than 100°. These units were made by Dr. Brown in the winter and early spring of 1910. My attempt at their reproduction was not begun until the fall of 1910. After three months' work, with the opportunity of counsel with Dr. Brown, and under similar conditions, I was still unable to reproduce light-negative units. I did make one that for a time had an extremely low negative sensibility. Its resistance was about 25,000 ohms. All other units that were crystallized by this method were of very low sensibility. The possible variations in conditions and the length of time required to make one unit conspired to make the search for the proper conditions a tedious one. The conditions essential to the successful manufacture of the light-negative units are yet unknown.

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[1] "Unit" is used in this paper in preference to "cell."

[2] Phys.-Zeitschr., Vol. 9, 1908, p. 569.

[3] Phys.-Zeitschr., II. (1910), 481, also PHYS. REV., XXXIII, p. 1, 1911.

Problem and Method.

In an attempt to get at the real nature of these cells their characteristics were investigated along the following main lines:

1. Variation of conductivity with intensity of incident light.
2. Variation of conductivity with time of exposure.
3. Variation in form of recovery curve with intensity of incident light.
4. Variation in form of recovery curve with time of exposure.

But one of the units at hand (made by Dr. Brown) could be used satisfactorily. Its resistance lay between 280 and 309 ohms. The best readings were all taken when this resistance was from 290 to 295 ohms.

The selenium unit was made one arm of a Wheatstone bridge. The resistances of the arms were approximately equal. The voltage across the selenium was always less than one volt. A sensitive galvanometer with a period of 2.6 seconds was used. It gave a deflection of 2.9 centimeters for each .1 ohm change of resistance in the selenium arm. The source of light was a forty-watt tungsten lamp, mounted upon a photometer bar. This sort of lamp was superior to a carbon lamp because it gave less radiant heat per candle power and showed less fluctuation of candle power with voltage. The constancy of candle power was obtained by constancy of voltage, an approximation sufficiently accurate.

To guard against outside disturbances several precautions were taken. To avoid moisture and sudden changes in temperature, the unit had been placed in a bath of paraffin oil upon manufacture, and was left there. The vessel containing the unit was placed inside a larger vessel, which was all blackened except a space directly in front of the sensitive surface of the selenium. The two vessels were placed inside a blackened pasteboard box. This box was suspended by a cord to cut off the effect of shocks or jars. To eliminate electrostatic induction, the outside of the box was covered with tin foil. The room was only partially darkened, but the selenium was properly shielded by screens of black paper placed on the photometer bar. Temperature readings were made by a thermometer placed in the oil just above and to the front of the sensitive surface of the selenium. The precautions stated above did not eliminate unsteadiness; in fact, whether or not they were of definite assistance was not ascertained.

With the selenium in the dark, the bridge was balanced as closely as convenient. The deflection was read, and then the light from the lamp, which was at a given distance, was suddenly thrown upon it, and the deflection of the galvanometer read every few seconds during the period of exposure. Periods of exposure lasting one, two, and three minutes were taken, after which the light was suddenly cut off, and in each case the galvanometer deflections were read every few seconds during the first one or two minutes of recovery. Two or three complete sets of readings were taken for each time of exposure at the given distance, and then the lamp was moved out to such a position that the intensity would be one half its first value, and the same operation repeated. The law of inverse squares could be applied without serious error due to area of source. Four such positions of the lamp were used and much time spent in trying to get readings at a fifth position, but the cell had become so unsteady that this could not be conveniently done. The temperatures and initial resistances were recorded for each exposure.

Experimental Work.

Unsteadiness.—At the outset difficulty was encountered, for the selenium under observation had no definite steady resistance even in the dark. At times there were small rapid variations in resistance, amounting to something like one or two tenths of an ohm in either direction. At other times the unsteadiness of the selenium manifested itself in long gradual shifts of resistance, which might take place in either direction with apparently equal ease. These long steady sweeps might amount to as much as one, two, or even three ohms. If one considers that the largest effect produced by the influence of light was a change of only five tenths of an ohm, the impossibility of taking readings when the cell is in an unsteady state will be apparent.

When work was first begun upon the cell, its periods of instability were not very frequent, and consequently not very annoying, for it was noted that when the cell remained steady before the light was thrown upon it, it seldom became more unsteady upon exposure. After the selenium had been used for two or three weeks the time between steady periods became longer and longer.

In general, a jar caused an increase in resistance, although it hastened the recovery to dark conductivity after an exposure was made. A sudden change in temperature made the unit extremely unstable, causing the conductivity to change back and forth in a most irregular manner. The temperature changes undergone during the night time may have accounted for the fact that the selenium was found to be more stable in the afternoon. The unsteadiness could scarcely have been due to loose contacts external to the unit.

When all disturbances were guarded against as thoroughly as possible there still remained an instability which must be due to something in the selenium structure itself.

Results.

Light-Negative Action.—In Fig. 1 a portion of the data is plotted. The heavy vertical line indicates the time at which the light was cut off. This figure shows the three-minute exposure curves with the four different intensities of light used. It will be seen that in only a few cases do the curves exactly agree with one another during the exposure, while during the recovery even a wider disagreement is shown. Therefore, before any generalizations could be drawn the mean curve had to be determined.

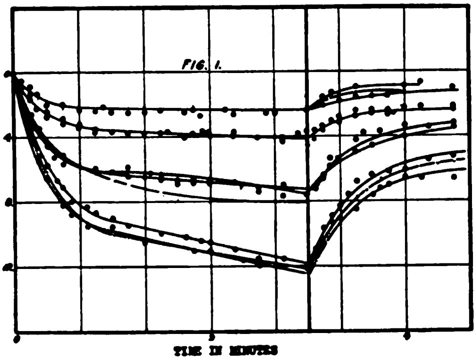

Fig. 1.

Through the points in the curves so drawn, the best smooth curve possible was drawn for each single exposure and recovery, and from these curves the centimeter deflections were read for the times 10, 20, 40, 60, etc., seconds after exposure, and for the same times after the light had been cut off. From these values of the deflection, and from the initial value of the conductivity in the dark, the percentage change of conductivity was computed for each deflection so read. The mean percentage change of conductivity for the given times, at the given intensities, were determined and plotted as the ordinates in the curves of Fig. 2. It is evident that the deflection after an exposure of one minute should be the same, whether the light were thrown off at the end of that minute or left on for a longer time, and hence for the one-minute curves of Fig. 2 an average has been taken of the percentage change observed during the one-minute exposure, together with the same observed during the first one minute of the two- and three-minute exposures. Likewise, for the two-minute curves an average was taken of the values obtained during the two-minute exposure with those obtained during the first two minutes of the three-minute exposure. Of course this was not possible in case of the recovery curves, so the recovery curves are each simply the average of two or three sets of observations, while, for instance, the one-minute exposure curves are each the average of as many as eight sets of observations.

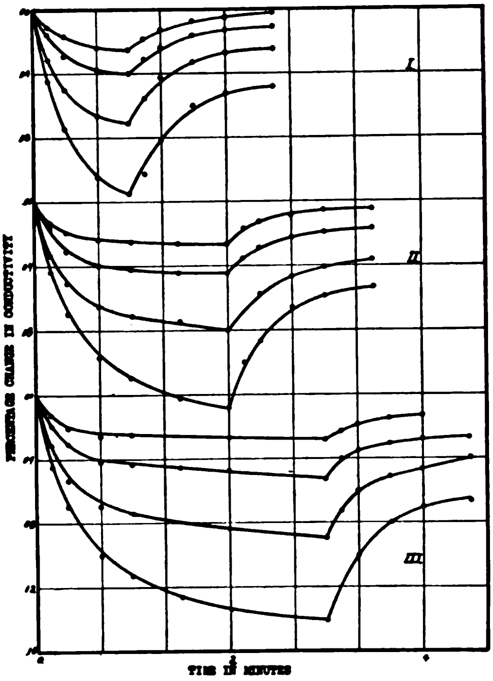

Fig. 2.

The curves given in Fig. 2 show several points. The more intense the incident light (the intensities are shown by indicated points in Fig. 3),

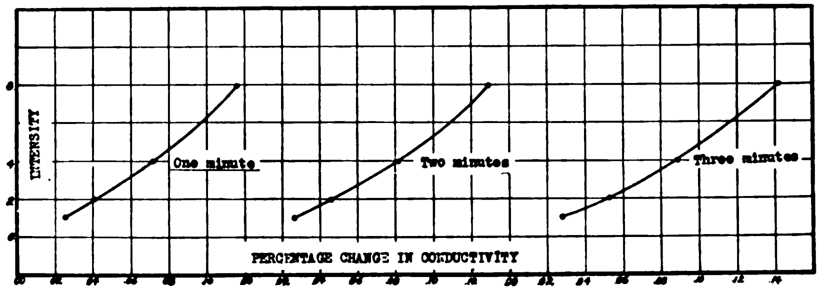

Fig. 3.

the greater is the total change in conductivity for a given period of exposure. With an intensity one half as great the change in conductivity observed is more than one half as great. The curves of Fig. 3 show the relation between the percentage change of conductivity and the intensity of the incident light, for periods of exposure of one, two, and three minutes respectively.

As to what relations we should have expected from consideration of the light-positive cells it would be hard to say, considering the various formulæ that have been established by different investigations.[1]

However, I have replotted my curve between change of conductivity at the end of three-minute exposure and intensity, using the distances from the source as abscissæ, so this curve might be compared with a similar one of Carpini reproduced by Ries. Curve I., Fig. 4, is the partial curve on an enlarged scale for the light-positive unit of Carpini, while Curve II. shows the light-negative one used in this investigation.

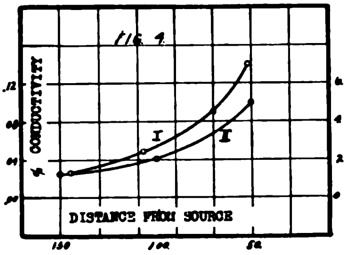

Fig. 4.

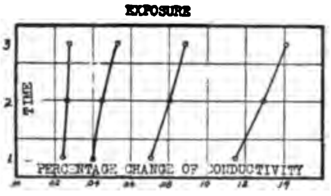

Fig. 5.

The two curves are in general the same shape, in fact, the agreement between the action of the light-negative and that of the light-positive units, under exposure to light of various intensities, is quite as close as that between two samples of light-positive selenium.

We also see that the longer the time of exposure the greater is the total change of conductivity for a given intensity of exposure. The relation between the conductivity change and the time of exposure for the four different intensities investigated are given in the curves of Fig. 5.

Another thing which seems apparent from the shape of the curves is that the less intense the light, the more quickly does a given per cent. of the total change take place, that is, the more quickly does the conductivity-time curve become parallel to the time axis. To show more plainly that this is true the scale to which each curve is plotted has been changed until, at the end of three minutes exposure the change in conductivity, so plotted, comes to the same point for all four intensities.

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[1] See Chap. VIII., Ries, Die Elektrischen Eigenschaften und die Bedeutung des Selens für die Elektrotechnik.

Curve I., Fig. 6, represents the change produced by the action of the faintest light, while Curve IV. represents that produced by the action of the most intense light.

The recovery curves are seen to be, in general, the reverse of the exposure curves, sloping sharply at first, and then more and more slowly approaching the original value of the conductivity in the dark. The greater has been the total change, the less complete is the recovery within a given time after the light has been cut off. Curves in Fig. 7 show that when the scales of plotting have been reduced, as in Fig. 6, for the exposure curves, that the same per cent. of the total recovery is reached first where the total change has been least. This is an effect similar to that shown in Fig. 6 for exposure to lights of different intensities.

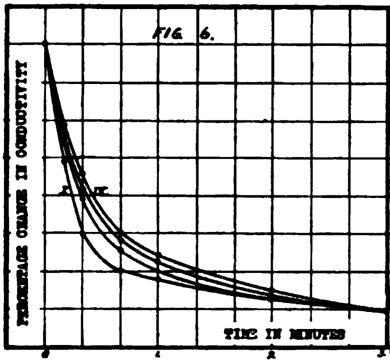


Fig. 6.

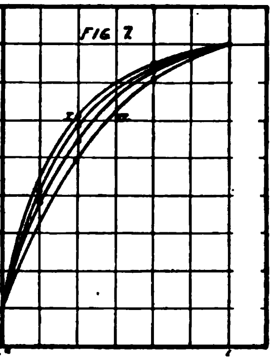


Fig. 7.

Curve I., Fig. 8, shows the percentage change in conductivity after the selenium has been allowed to recover for one minute from an exposure of one minute, plotted with the intensity of the light to which it has been exposed. Curves II. and III. show the same for one-minute recoveries from exposures of two and three minutes respectively. These are all long, slightly concave, curves.

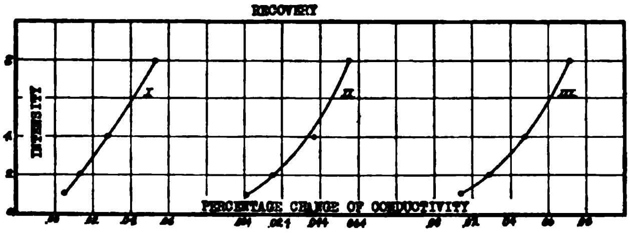


Fig. 8.

The next set of curves shows the percentage change in conductivity after the selenium has been allowed to recover for one minute from an exposure to lights of given intensities, plotted against the time of exposure. Curve IV., Fig. 9, represents the relations for an exposure to the most intense light, while Curve I. represents the same for an exposure to the least intense light. These are also long curves, but are slightly convex.

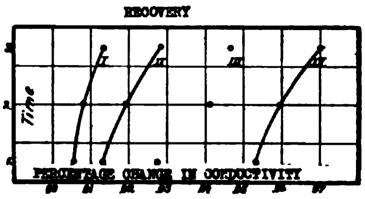
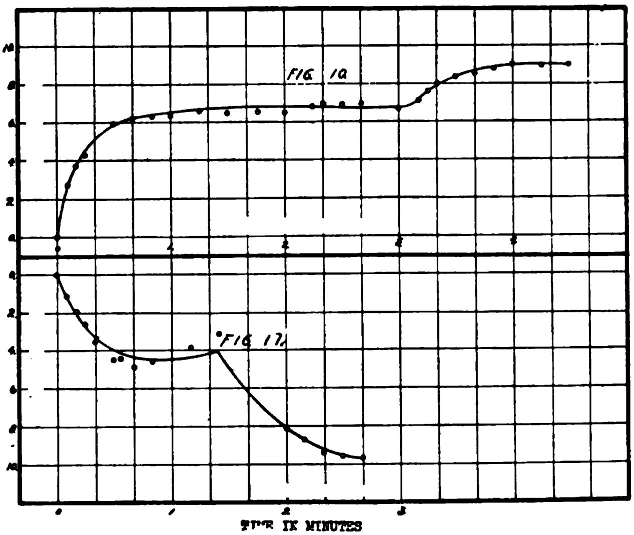


Fig. 9.

While the curves of Figs. 8 and 9 are not of the same shape, yet the curvature is so slight in each case that, in general, they show an agreement in the light-negative units with the facts found by Miss Louise McDowell in regard to the Bidwell type of light-positive units. She states[1] "the effect of increased duration of excitation upon the form of recovery curve is similar to the effect of increased intensity."

Light-Positive Action.—When the unit was first put in use several weeks elapsed before it was observed to act at any time as a light-positive unit.[2] But as the work progressed this happened an increasing number of times, until, in all, eleven cases of this light-positive action were recorded. Some of these positive deflections were followed closely. Fig.



Figs. 10–11.

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[1] Physical Review, XXIX., p. 35, 1909.

[2] Brown in an article previously cited reports this light-positive action as occasionally observed in some of the other units.

10 shows the form of one type of action, both after the light has been thrown upon the selenium, and after it has been cut off. The exposure curve is of the form of the regular exposure curves observed with a Ruhmer unit, while the conductivity curve after the light is off reminds one of the recovery curve for the light-negative unit. At least three such cases as this occurred.

After plotting this curve, the occurrence of its exact opposite was recalled, and its appearance watched for. It was never caught, however, except in the case of the partial curve plotted in Fig. 11. Here the exposure curve is of the light-negative form, while the recovery curve is similar to that of the light-positive unit.

One surprising thing about this light positiveness in the light-negative unit is the ease and suddenness with which it comes and goes, leaving no trace of itself. The table below will show this point well.

	Time.	Interval.	Resistance in Ohms.
Fig. 4. Curve II. Negative....	5:56	6 min.	291.01
Fig. 10. Positive.....	6:02	11 min.	290.97
Fig. 4. Curve III. Negative	6:13		290.7

It is seen that a perfectly regular light-negative curve was taken, then within a period of six minutes the light-positive curve of Fig. 10, while within another period of eleven minutes it has regained its former character and gave another perfectly regular light-negative curve.

It seems that all this simply shows how nearly this selenium is existing in the two forms at the same time. In the earlier part of this article we noted how the high resistance selenium had a high sensibility, and how the sensibility decreased with resistance through several types. Now if we can think of the resistance becoming so low that the sensitiveness passes through a zero point, and then to a negative value, we can understand how the units whose negative sensitiveness is as low as that of the one we are discussing, would be existing so close to the border line of sensitiveness that the sudden darkening or lighting might be a sufficient stimulus to throw from one form over into another.

A second unit of resistance close to five hundred ohms was set up, but it was found that it was even more unsteady than the unit of three hundred ohms which had been used. Perhaps this might have been expected, for the higher resistance would seem to indicate that this unit was existing still closer to the border line of sensitiveness than the former one.

Impurities.—The question first asked when the light-positive action of selenium was discovered was whether or not the whole effect was not due to the presence of an impurity such, perhaps, as a selenide formed by the selenium and the metal of the electrode. Pfund[1] answered this question by making sensitive units using carbon, which will not combine with selenium, as his electrodes.

In the manufacture of his units, Dr. Brown used German silver wire which the selenium attacks to some slight extent, but the cells of Ries which approximate those of Brown were made with carbon electrodes. No attempt has yet been made to manufacture the light-negative units using carbon.

The striking similarity which we find between the action of the light-negative and that of the light-positive selenium makes it probable that this negative effect is due to some peculiar structure of the selenium itself, or due to an impurity which will act in a similar manner to the selenium. It may be that if impurities affect the manufacture of these units they act simply to aid in the formation of the crystals or an arrangement of them such as may be necessary to cause light-negative action. Indeed, this seems the more reasonable, for selenium is unique in its sensibility to light.

Temperature Effect.—In this limited investigation nothing was attempted to show the effect of differences in temperature upon the dark resistance of the selenium, yet with each observation the temperature and dark resistance were both recorded in hope that some correction for temperature might be applied.

So irregular were the relations found between the two that no statement could be made in regard to the variation one with the other, whether we consider all the readings or only those for a single day. Brown[2] shows that within certain limits the conductivity is increased by a rise of temperature.

SUMMARY.

It is impossible to make any general statements concerning light-negative selenium, but so far as the selenium unit here investigated is concerned, the following conclusions are in agreement with experiment:

I. The making of light-negative selenium seems to require very particular conditions which were not ascertained after several months of effort.

II. The resistance of the light-negative selenium is very unsteady, both in the light and in the dark.

A sudden jar or a sudden change in temperature adds greatly to this unsteadiness.

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[1] Phil. Mag., Vol. 7, p. 26, 1904.

[2] Phys. Rev. XXXIII, p. 1, 1911.

III. The change in conductivity of the light-negative selenium when exposed to light is very small, being less than one per cent.

IV. Exposure Curves:

1. Change of conductivity increases with increased intensity of light, but not proportionately.
2. Change in conductivity increases with time of exposure, rapidly at first, and then reaches a nearly steady condition.
3. With a faint light the larger per cent. of the total change takes place within the first few seconds of exposure.

V. Recovery Curves:

1. In general, they are the reverse of the exposure curves.
2. The more intense the light to which the selenium has been exposed the less complete is the recovery in a given time after the light has been removed.
3. The longer the selenium has been exposed to the light the less complete is its recovery within a given time.
4. The less has been the total change in conductivity during exposure the greater is the per cent. of recovery taking place in a given time.

VI. Sensibility of the light-negative selenium seems to exist so close to the border line of sensitiveness that a slight stimulus will completely change its sign.

VII. The evidence indicates, but does not prove, that the negative effect is due to the selenium structure itself and not to an impurity present.

I wish to express my thanks to Professor G. W. Stewart, under whose supervision these experiments were conducted, and also to Professor F. C. Brown for his kindly interest in the progress of the experiments.

Physical Laboratory,
State University of Iowa.

REFRACTIVE INDEX OF METALS.

By P. A. Ross.

THE investigation here described has to do with the determination of the refractive index of metals by three different methods. Two of these methods involve the use of metallic prisms deposited upon glass. In depositing these prisms the cathode discharge from a wire was employed. By proper care a very regular double prism could be built up by the disintegration of the metal wire.

The vacuum tube employed is shown in Fig. 1 and was composed of a brass tube about five inches long by three and one half inches in diameter and having flanged ends. These flanges were carefully ground to give a good plane surface. This surface was coated with a beeswax and vaseline mixture and two plate glass discs (*a*) and (*a*′) firmly pressed on. When the air was exhausted the plates drew down, securely sealing the tube. One of the glass discs (*a*′) had a small hole drilled through it and a cathode cemented into this. A wire or narrow ribbon of the metal to be deposited could be attached to this so as to project along the axis of the tube. From the large tube (*b*) a small tube (*d*) led to a Gaede mercury pump.

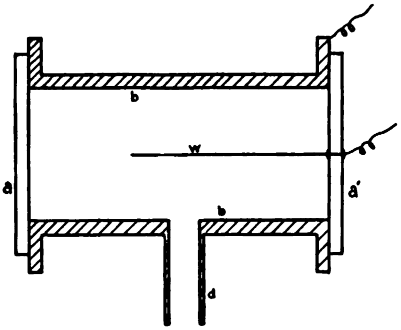

Fig. 1.

A plate of glass which was first carefully chemically cleaned was placed parallel to the wire cathode and about a millimeter below it. In Fig. 2, *w* represents an end view of the wire and *p* the glass plate. After the tube was exhausted to a pressure of .01 to .001 mm. of mercury a current from an induction coil was sent through it in such a manner that the wire was the cathode while the brass tube (*b*) (Fig. 1) served as an anode.

It was found that while a round wire gave prisms of the largest angle they usually had curved faces. A thin ribbon or wedge made by flattening a wire or cutting a strip from a sheet of metal gave the most uniform prisms. In any case a comparatively small number of the prisms made were usable.

The rate of deposition varied greatly for different metals. Copper, silver, gold, lead, platinum and bismuth deposited quite rapidly. That is, a prism of sufficient thickness could be obtained in from twenty to forty minutes. Iron required several hours. Magnesium was exceedingly slow, taking several days. The magnesium prism had to be deposited in a very high vacuum after the tube had been washed out with hydrogen. It was completely ruined after being exposed to the air for a few hours.

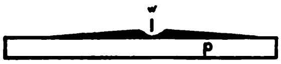

Fig. 2.

The prisms were apparently of a cross section similar to that shown in Fig. 2. Directly underneath the ribbon almost no metal was deposited.

All prisms were deposited on plate glass of about 5 mm. thickness. The glass was first carefully tested to see that the faces were plane and parallel.

Method of Measurement.

The first method of carrying out the measurements upon the prism was the same as used by Kundt.

The spectrometer used was one made by Krüss, of Hamburg, having a ten inch circle and provided with micrometer microscopes reading to seconds. As a usual thing it was impossible to set the cross wires of the telescope to within from one to four seconds of a constant reading.

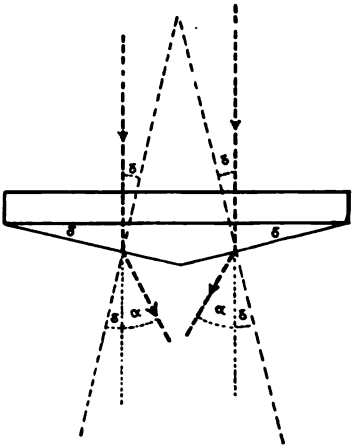

Fig. 3.

Paper masks were cut out and put over the face of the prism to cover the thin central line and all other portions of the prism that did not give a sharp image of the cross wires in the Gauss eyepiece.

In determining the deviation there was the same difficulty found by Kundt, *i. e.*, the images of the slit were never quite sharp, but had slightly diffuse edges.

The deviation measurements were made for three colors of light, red, yellow and blue. The red was obtained by passing light from a "student" kerosene lamp through two thicknesses of deep red glass. It gave a mean wave length of $620\mu\mu$. The yellow light was obtained from a sodium burner. The blue light was obtained by passing light from a "student" kerosene lamp through two thicknesses of blue glass. It approximated to a wave length of $450\mu\mu$.

The prism angle was measured in the usual way with a Gauss eyepiece. In measuring the deviation the glass side of the prism was toward the collimator and perpendicular to it as indicated in Fig. 3. Then the only deviation was at the emergence of the light from the metal prism. Then δ, the angle of incidence (metal to air), is equal to the prism angle. The angle of emergence is $\delta + \alpha$ where α is the deviation. Then

$$N = \frac{\sin(\delta + \alpha)}{\sin \delta}.$$

Since very small angles are proportional to their sines the equation becomes $N = \frac{\delta + \alpha}{\delta}$, as used by Kundt.

The readings given below for copper prism No. 1 are fair samples of the accuracy obtained in reading the prism angle and the deviation of the refracted light. The readings grouped under a single bracket and marked *A*, *B*, etc., were made on the same day. The different groups indicated in this way were made at intervals of several days.

Copper Prism No. 1.

Prism Angle, δ.	Deviation, α.		
	Red.	Yellow.	Blue.
12″	− 7″	− 6″	0″
15″	− 6″	− 7″	−4″
A 16″	− 7″	− 7″	−3″
13″	−10″	− 7″	−4″
13″	− 9″	− 8″	−4″
14″	− 7″	− 7″	−3″
17″	−10″	− 9″	0″
B 16″	− 6″	− 9″	−4″
16″	− 9″	− 9″	−2″
13″	− 9″	−10″	−2″
17″	− 7″	− 7″	−2″
16″	−11″	−11″	−4″
C 16″	−11″	− 8″	−3″
18″	−12″	− 9″	−4″
18″	− 9″	−10″	−2″
15.3″	− 8.6″	− 8.3″	−2.6″

$$N\,(\text{red}) = \frac{\sin(\alpha + \delta)}{\sin \delta} = \frac{\alpha + \delta}{\delta} = .44,$$

N (yellow) = .46,

N (blue) = .83.

Below is given a summary of the refractive indices of the different prisms as determined by the method of deviation.

	Red (620).	Yellow (589)	Blue (450).
Copper (1)	.44	.46	.83
Copper (2)	.40	.57	.85
Copper (3)	.45	.56	.93
Copper (4)	.43	.48	.88
Copper (5)	.43	.55	.97
Iron (1)	1.96	1.85	1.42
Iron (2)	2.34	1.85	1.55
Lead (1)	2.38	1.95	1.71
Lead (2)	2.43	1.94	1.81
Platinum (1)	2.05	1.80	1.56
Platinum (2)	2.05	1.88	1.50
Platinum (3)	2.07	1.75	1.47
Silver (1)	.35	.34	.22
Silver (2)	.37	.28	.21
Zinc	2.39	2.11	1.79
Magnesium	.51	.40	.26
Gold (1)	.35	.58	.98
Gold (2)	.39	.65	1.02
Bismuth (1)	1.78	1.98	2.20
Bismuth (2)	1.78	1.92	2.30
Nickel	1.90	1.88	1.77
Brass	.45	.66	1.04

The values for brass are practically identical with those obtained for copper. It would seem that the prism was really a copper prism. The wire from which it was deposited was grayish after the deposition of the prism. The copper may have simply left the zinc behind. All copper prisms deposited very rapidly while zinc deposited very slowly.

MEASUREMENT OF REFRACTIVE INDEX BY INTERFERENCE.

Some of the prisms deposited from gold, silver, copper and iron and one of the platinum prisms gave plain interference fringes in reflected light. Other prisms from the same metals and apparently deposited under identical conditions did not. Copper and iron seemed to be especially apt to form prisms crossed by beautiful interference fringes. This suggested that these prisms might be made of metallic oxides instead of the pure metal, but the fact that such difficultly oxidizable metals as gold and platinum also formed such prisms indicated that this could not be the true explanation of their formation. Also prisms showing interference fringes were formed even after the apparatus had been washed out with a stream of hydrogen from a hydrogen generator. The prisms showing interference also gave values of the refractive index which were in good agreement with those obtained by the deviation method from those showing no interference.

Since the measuring of the deviation is the most difficult and inaccurate step in the determination of the refractive index of a prism it would be a distinct advantage to use measurements of the distance apart of these fringes instead of measuring the deviation.

No prism showed more than two fringes before becoming so thick as to be absolutely opaque; therefore the prisms were all less than one light wave in thickness. Since the prism angle was so small, the fringes were rather far apart and broad. Their breadth made it hard to determine the exact distance from center to center of the bands.

If λ = wave length in air of the light used,

λ_s = wave length of the same light in the substance considered.

Then

$$\frac{\lambda}{\lambda_s} = N \text{ (refractive index).}$$

If the substance is in the form of a prism having plane faces and an angle δ between them, as indicated in Fig. 4, the fringes will occur at intervals of $\lambda_s/2$ increase in thickness. Let d be the distance between fringes. Then

$$\tan\delta = \frac{\lambda_s}{2d}$$

and

$$N = \frac{\lambda}{2d\tan\delta}.$$

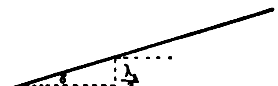

Fig. 4.

The distance d between fringes was measured by means of a micrometer microscope. The prism was placed on a table and over it a plate of glass (g) inclined at an angle of 45° so as to give illumination at normal incidence from a light placed at one side of the microscope (M). This arrangement is shown in Fig. 5. The microscope was focused on the fringes and the distance between the fringes measured.

The angle of the prism was measured in the usual way with a Gauss eyepiece and also by placing it on the table of a spectrometer, allowing light from the collimator slit to fall on the faces of the prism and measuring the separation of the two images of the slit as seen through a telescope mounted on the carriage of a dividing engine at a distance of about 657 cm. from the prism. The distance between the images of the slit divided by the distance from the prism to the telescope gave the tangent of four times the prism angle.

Then if L = distance from prism to telescope;
l = displacement of the dividing engine carriage;
δ = prism angle;
d = distance between interference bands;
λ = wave length (in air) of the light used;
N = refractive index;

$$\tan\delta = \frac{l}{4L};$$

$$N = \frac{\lambda}{2d\tan\delta}.$$

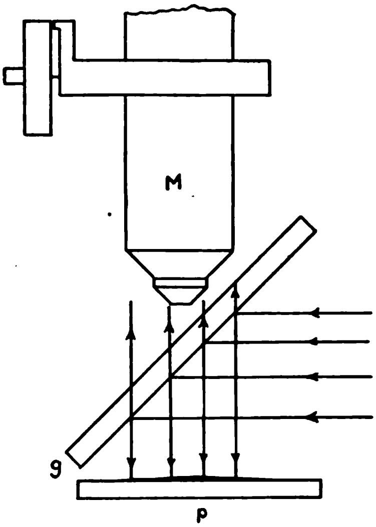

Fig. 5.

The date given below for copper prism No. 2 and silver prism No. 2 are fair samples of the accuracy attainable by this method. It will be seen that the method is approximately one decimal place more accurate than the deviation method.

Copper Prism No. 2.

l	L	Distance between Bands (d).		
		Red.	Yellow.	Blue.
4.04 mm.	6,573 mm.	4.85 mm.	3.59 mm.	1.45 mm.
4.04		4.83	3.56	1.44
4.00		4.83	3.60	1.44
4.12		4.86	3.58	1.48
4.12		4.83	3.59	1.45
4.12		4.83	3.56	1.45
4.08 mm.		4.84 mm.	3.58 mm.	1.45 mm.

$$\tan \delta = \frac{l}{4L} = \frac{4.08}{6573 \times 4} = .0001533,$$

$$N_y = \frac{\lambda}{2d \tan \delta} = \frac{.000589}{2 \times 3.58 \times .0001533} = .529,$$

$$N_r = .414,$$

$$N_b = 1.005.$$

Silver Prism No. 2.

l	L	Distance between Bands.		
		Red.	Yellow.	Blue.
4.21 mm.	6,573 mm.	4.20 mm.	6.15 mm.	5.12 mm.
4.21		4.21	6.15	5.11
4.18		4.19	6.17	5.12
4.19		4.18	6.15	5.12
4.19		4.22	6.14	5.09
4.22		4.22	6.14	5.09
4.200 mm.		4.203 mm.	6.150 mm.	5.111 mm.

$N_r = .461$ $N_y = .299$ $N_b = .274$

Below is given a summary and comparison of the refractive indices determined by the interference method and the deviation method for the same prisms.

	$\lambda=620$		$\lambda=589$		$\lambda=450$	
	Interf.	Dev'n.	Interf.	Dev'n.	Interf.	Dev'n.
Copper (2)	.414	.40	.529	.57	1.005	.85
Copper (3)	.455	.45	.508	.56	.908	.93
Copper (4)	.388	.43	.517	.48	.942	.88
Gold (1)	.460	.35	.658	.58	1.094	.98
Platinum (3)	1.94	2.07	1.60	1.75	1.49	1.47
Iron (2)	2.04	2.34	1.86	1.85	1.60	1.55
Silver (2)	.461	.37	.299	.28	.274	.21

Refractive Index by Newton's Rings.

In ordinary cases Newton's rings seen by reflected light have a dark center, caused by a retardation of $\lambda/2$ at one surface over that at the other with no difference of path. This change of phase is due to a thin film of air between the lens and plate.

Young showed that if sassafras oil were introduced between a lens of crown glass and a plate of flint glass a light center was obtained with reflected light. Since sassafras oil is intermediate in optical density between flint and crown glass the change of phase is the same at each reflecting surface. Accordingly if the substance between the lens and plate be between the two in optical density the interference rings have a light center. This can be made to furnish a rough test of the refractive index of metals.

With air, crown glass lens and sodium light at normal incidence the following metals gave light centers: Silver, gold, copper, magnesium.

The following metals give dark centers with sodium light: Platinum, iron, nickel, lead, tin, zinc, bismuth, aluminum.

Then silver, gold, copper and magnesium have refractive indices less than unity for sodium light. Platinum, iron, nickel, lead, tin, zinc, bismuth and aluminum have refractive indices greater than unity.

By substituting liquids of known refractive index for the air film it is possible to carry this rough determination somewhat further. Unfortunately as the refractive index of the liquid approaches that of the metal the reflection falls off to such an extent that the rings become too dim for accurate work.

Iron has a refractive index greater than CS_2 (1.63) for sodium light and red light. Aluminum and tin both lie between water (1.33) and CS_2 (1.63). Platinum, lead, zinc and bismuth are all greater than 1.63.

In conclusion I wish to thank Professor Sanford for his advice and assistance in this work.

STANFORD UNIVERSITY.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

A NEW VIRIAL THEOREM.[1]

BY D. F. COMSTOCK.

IT can readily be shown that the electric energy of a hollow charged sphere is equal to the mechanical stress in the substance of which the sphere is made integrated over the surface of the sphere. The stress is of course caused by the mutual repulsion of the various elements of charge.

It can also readily be shown that if a hollow box could have perfectly reflecting walls and be filled with radiation and left to itself, the integral of the stress caused by radiation pressure over the whole surface of the box would be equal to the total contained energy of radiation.

In both of the above cases what we might call the "mechanical stress integral" is equal to the total electromagnetic energy.

These two examples are in fact special cases of a general theorem which can be proved from the fundamental equations of electromagnetic theory. This theorem states that the mechanical stress integral plus an integral representing the stress-modifying reaction due to the inertia of the radiant energy present, is equal to the total electromagnetic energy of the system. The stress integral mentioned may fitly be called the "confining function."

The statement of the theorem is as follows:

$$\iiint (r \cdot F\sigma)d\tau + \frac{1}{4\pi c}\frac{d}{dt}\iiint r \cdot E \times H d\tau = \frac{1}{8\pi}\iiint (E^2 + H^2)d\tau,$$

where r = vector from origin to point P,

F = total electromagnetic force per unit charge at point P ($F = E + \frac{1}{c} v \times H$, where v = velocity of charge at point P),

σ = density of charge at P,

$d\tau$ = element of volume,

c = velocity of light,

E = electric force intensity at P,

H = magnetic force intensity at P.

The volume integrals must be taken so as to include the whole system. The first term on the left of the equation is very similar, except for the factor

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 14, 1911.

½, to the "virial" of Clausius, well known in kinetic theory. The confining function might therefore be called the electromagnetic virial. Since the second term on the left is a time derivative it will drop out of the equation when we take an average over a long time *provided* the system does not enlarge indefinitely and keeps its same average position. This corresponds to the "stationary motion" of Clausius. In this case the new virial is equal to the *total* energy, while the Clausius virial is equal to the *kinetic* energy.

A simple example of the above case is that of the hollow, totally reflecting sphere mentioned at the beginning, and it is easy to verify the general theorem in this case. Since the pressure of radiation after equilibrium is one third the energy density (e), the virial is

$$\left(r \cdot \frac{e}{3}\right) 4\pi r^2 = e \cdot \text{volume of sphere} = \text{total energy}.$$

It can readily be shown that the virial is equal to the stress-integral over a volume, a surface or a line according as the shape of the confining structure be considered as three, two or one dimensional. Indeed,

$$\iiint (r \cdot F\sigma)d\tau = \iiint (X_x + Y_y + Z_z)d\tau,$$

where, using the familiar symbols of the theory of elasticity, X_x, Y_y, and Z_z are the tensions within the confining structure.

To take a "one-dimensional" illustration, the *mutual* energy of two similar point charges is q^2/r, where (q) is charge and (r) distance between them. If they are held in place by a thread joining them the tension in this thread will be the force between charges, namely, q^2/r^2, and the integral of the tension will be

$$r \cdot \frac{q^2}{r^2} = \frac{q^2}{r} = \text{mutual energy}.$$

A NEW FORM OF GOLD-LEAF ELECTROSCOPE: A NULL INSTRUMENT.[1]

By J. C. Hubbard.

A GOLD-LEAF L is suspended in the electric field between two brass plates insulated from each other and connected to the terminals of a suitable constant potential battery (50 to 200 cells). The middle of the battery is earthed. The gold-leaf and the field-plates are enclosed in a brass case which is also earthed. Connected rigidly to the case is a framework into which a microscope may be adjusted so as to focus through a small glass window in the front of the case upon the edge of the gold-leaf. Coincidence of the image of a point in the edge of the earthed leaf with a cross-hair parallel to the image of the leaf in the microscope provides the zero of the instrument. The case, contents, and microscope are capable of rotation as one body about a horizontal axis parallel to the axis of rotation of the leaf. When the leaf is charged the instrument is rotated in the same sense as the deflection of the leaf until the image of the point in the edge of the leaf again coincides with the cross-hair, *i. e.*, until the leaf is in its original position with respect to the field-plates. Fine adjustment of the rotation is made by means of a tangent screw not shown in the figure.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 14, 1911.

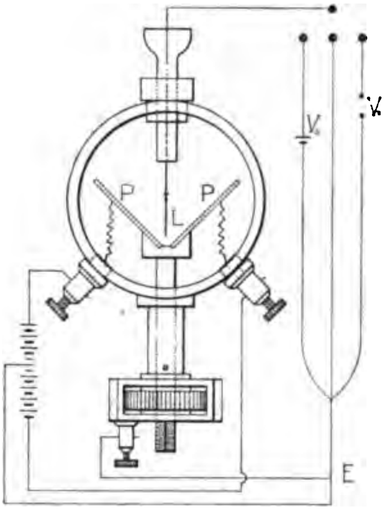

Fig. 1.

Since at any point in the leaf the electric force is, by the manipulation just described, proportional only to the potential applied to the leaf and always in the same direction with respect to the leaf (assuming the field uniform), and since the resultant of the electric force and gravity must lie in the plane of the leaf, we have

$$V = k \sin \phi,$$

where V is the potential applied to the leaf, k is a constant depending on the potential of the field-plates, gravity, the thickness of the leaf and the dimensions and design of the instrument (*i. e.*, k is a constant to be determined by calibration), and ϕ is the angle through which the instrument was turned to bring the leaf to its initial position with respect to the field-plates.

Table I.

V	ϕ	k	V	ϕ	k
1.0184	19′.7±.2	178	5.00±.05	1° 36′.6	178
.408	7 .8 "	179	9.48 "	3 3 .5	178
1.224	23 .5 "	179	13.82 "	4 24 .5	180
2.448	46 .8 "	180	18.76 "	5 59 .1	180.4
4.896	1° 33 .0 "	180.8	24.00 "	7 39 .2	180.1
6.120	1 56 .7 "	180.5	31.12 "	9 56 .4	180.2

The formula assumes, as we have said, that the field is uniform, *i. e.*, that the plates are parallel. An instrument in which this condition was fulfilled was constructed. The results given in Table I. are typical. The plates were 14 mm. apart and charged to $+$ and $-$ 50 volts respectively. In the first column of V's the potential in volts was measured by potentiometer, in the second, by voltmeter.

The deviations in k are well within the errors of observation, which are indicated in the table. The electroscope so constructed has the disadvantage that when a fairly large potential is applied to the leaf the latter is apt to fly to one of the field-plates and adhere, unless the field-plates are so far apart as to greatly diminish the sensibility. In taking the above series, 20 volts was the largest potential which could without great inconvenience be applied to the leaf. Very great sensibilities are possible in this form of the instrument by adjusting the plates closer together and increasing their difference of potential, and the instrument so used is ideal for the measurement of small differences of potential or for slow fluctuations of larger magnitude.

To make the instrument more convenient for rapid work over a wider range the form shown in the figure was constructed, in which ample clearance is afforded the leaf. Typical results are shown in Table II.

TABLE II.

V (volts).	ϕ	k
6.1	49.8	422
14.3	1° 56.6	422
31.8	4 18.6	423
51.4	7 0.8	421
71.5	9 48.9	419
90.2	12 24.8	420
106.5	14 46.0	418

A small, though systematic change in k is noticeable at the higher potentials, amounting, as may be seen, to 1 per cent. The systematic variation in k has been observed in all cases where ϕ is greater than 10° and is due to the non-uniformity of the field causing a very slight curvature in the leaf.

The instrument in this form is a most convenient device for the rapid measurement of potentials, the sensibility being almost instantly adjusted to any desired value by turning the graduated nut which raises or lowers the field-plates. Adjustment of the microscope to give an unchanged zero with the field on or off insures a perfectly definite sensibility for any reading of the nut. As an illustration, the sensibility was so adjusted that $k = 200$. Since for small angles we may take $\sin \phi = \phi$, a deflection (d) of 1 cm. on the scale at 1 meter used in reading the angles of tilt (telescope and scale method) corresponds to 1 volt. Table III. shows the results of a rapid comparison of cells which had been previously compared by the potentiometer method.

The principal utility of the electroscope or sine electrometer here discussed consists in its being a null instrument giving angular readings, the sines of which are strictly proportional to the potentials applied to the leaf. One reading with a standard cell is thus sufficient for calibration. The various possible ranges in one instrument make it suitable for radio-activity and gas conductivity experiments as well as for measurements in atmospheric electricity where relatively high potentials may be encountered. The accuracy depends upon the magnifying power of the microscope and upon the means for reading the angle of tilt. Much may be hoped for from improved design.

TABLE III.

Cell.	V	d (cm.).
Weston	1.018	1.02
Dry cell	1.474	1.47
Storage cell	2.016	2.02
3 storage cells	6.097	6.08

It should be further noticed that the instrument has a *constant and very small capacity* for any deflection, making it available for the comparison of small capacities by the method of divided charge.

CLARK COLLEGE,
WORCESTER, MASS.

SPECTRAL LUMINOSITY CURVES DETERMINED BY THE METHOD OF CRITICAL FREQUENCIES.[1]

BY HERBERT E. IVES.

SPECTRAL luminosity curves obtained from determination of the speed of disappearance of flicker (light against darkness) have been supposed to be similar to those obtained by the flicker photometer (alternation of two lights under comparison). The method of critical frequencies has however been found to give a Purkinje shift (increase of brightness of blue) as the illumination is decreased, while the results of the author with the flicker photometer show that method to exhibit a reversed Purkinje shift (increase of brightness of red). With the same apparatus as previously used the two methods have been compared and agree in both showing the reversed Purkinje effect. At very low illuminations, however, the method of critical frequencies shows a shift in the opposite direction, or true Purkinje effect.

It has been found by Porter that if log. illumination is plotted against critical frequencies, with white light, a straight line results. At about .25 meter candles the line abruptly changes its direction, perhaps due to change from cone to rod vision. Upon plotting in this manner the illuminations at which the present results were obtained, the reversed Purkinje effect is found to hold above the bend in the straight line, the Purkinje effect below.

Attention was then turned to securing the relation between log I and critical frequency for the different spectral colors. Red light plots as a straight line without bend, blue light as a straight line which bends to the horizontal, that is, the critical frequency becomes independent of illumination. Consequently the relative inclination of red and blue lines changes, giving the two kinds of Purkinje effect.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 14, 1911.

The question whether the flicker photometer might be considered as a simple dove-tailing of two flicker sensations each following the relation just discussed was next investigated. Apparently it is not, although the phenomena of critical frequency exert a dominating influence on the results with the flicker photometer.

Some experiments on the relative sensibility of the peripheral and central retina indicate that at high illuminations there is little difference. At low illuminations the periphery is more sensitive than the center to blue flicker, but for red flicker the condition is exactly reversed. The periphery quickly tires and possesses such advantage as it has for detecting flicker only for momentary observation. It is therefore unfitted for continuous photometric work. A large photometric field is always more sensitive to flicker than a small one.

ERRATA AND ADDENDA.

Page 259. To enable one to locate properly points platted in Fig. 12 in the paper by A. G. Worthing on Some Thermodynamic Properties of Air and of Carbon Dioxide, the following table is given:

μ and η for CO_2 at low pressures.

p in Atmos.	T in °C.	μ in Deg./Atmos.	η in Deg./Atmos.
Results of Joule and Thomson.			
1- 6	4.0	1.307	
	33.5	1.020	
	51.9	.883	
	91.8	.648	
	96.0	.639	
Result of Cazin.			
1- 5	10		.88
Result of Natanson.			
	19.7	1.18	
Results of Kester.			
1–40	.6	1.442	
	20.4	1.173	
	39.5	1.037	
	59.5	.948	
	79.5	.868	
	96.6	.786	
Result of Searle.			
5–10	0		.63
Results of Worthing.			
0	0	1.375	1.265
	30	1.065	.975
	50	.910	.830
	100	.595	.540
Results based on data by Chappuis and by Holborn and Austin.			
0	0	1.290	1.125
	30	1.108	.970
	50	.960	.850
	100	.575	.480
Results based on Clausius's equation and γ data by Worthing.			
	0	1.36	1.22
	30	1.06	.96
	50	.90	.81
	100	.61	.55

INDEX TO VOLUME XXXIII.

A.

Acoustic Shadow of a Rigid Sphere, with Certain Applications in Architectural Acoustics and Audition, *G. W. Stewart*, 467.

Addenda, 563.

Air, Some Thermodynamic Properties of, and of Carbon Dioxide, *A. G. Worthing*, 217, 563.

Alloys, The Optical Constants of, as a Function of Composition, *J. T. Littleton, Jr.*, 453.

Aluminum, The Positive Potential of, as a Function of the Wave-length of the Incident Light, *J. R. Wright*, 43.

American Physical Society.
  Minutes, 447.
  Abstracts, 448, 557.

Angell, M. F., Thermal Conductivity at High Temperatures, 421.

Arc Lamps, The Radiant Efficiency of, *Henry Phelps Gage*, 111.

B.

Binary Solution, On the Dissolution of a Metal in a, one Component Acid, *Arden Richard Johnson*, 27.

Bishop, Edwin S., An Absolute Determination of the Minimum Ionizing Energy of an Electron, and the Application of the Theory of Ionization by Collision to Mixtures of Gases, 325.

Book Reviews: 152, 452.

Brown, F. C., The Nature of Light Action in Selenium, 1.

Brown, F. C., A Method of Measuring the Fluctuations in a Rapidly Varying Resistance, 53.

Brown, F. C., The Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium, 403.

Brown, Joseph G., New Records of Sound Waves from a Vibrating Flame, 442.

Brownian Movements, A Verification of the Theory of, and a Direct Determination of the Value of *NE* for Gaseous Ionization, *Harvey Fletcher*, 81.

C.

Carbon, On the Fusion of, *O. P. Watts* and *C. E. Mendenhall*, 65.

Carbon Dioxide, Some Thermodynamic Properties of Air and of, *A. G. Worthing*, 217, 563.

Caswell, A. E., Determination of Peltier Electromotive Force for Several Metals by Compensation Methods, 379.

Clark, W. H., A Method of Measuring the Fluctuations in a Rapidly Varying Resistance, 53.

Cobalt, The Magnetization of, as a Function of the Temperature and the Determination of its Intrinsic Magnetic Field, *W. W. Stifler*, 268.

Comstock, D. F., A New Virial Theorem, 557.

Compton, Karl T., The Influence of Contact Difference of Potential on the Measurement of Electron Velocities in the Photoelectric Effect, 449.

Crum, Lilah B., Certain Characteristics of Light Negative Selenium, 538.

Crystallography, On the Nomenclature of, *Paul Saurel*, 203.

D.

Dellinger, J. H., Note on a Variable Low Resistance, 215.

Dissolution of a Metal in a Binary Solution, one Component Acid, *Arden Richard Johnson*, 27.

Distribution of Current and the Variation of Resistance in Linear Conductors of Square and Rectangular Cross-section when carrying Alternating Currents of High Frequency, 184.

Douglas, J. F. H., A Simple Proof of Poynting's Theorem, 232.

E.

Edwards, Hiram Wheeler, The Distribution of Current and the Variation of Resistance in Linear Conductors of Square and Rectangular Cross-section when carrying Alternating Currents of High Frequency, 184.

Electrical Resistance, Temperature Coefficients of, *A. A. Somerville*, 77.

Electron, An Absolute Determination of the Minimum Ionizing Energy of an, and the Application of the Theory of Ionization by Collision to Mixtures of Gases, 325.

Electron Theory of Contact Electromotive Force and of Thermoelectricity, *O. W. Richardson*, 448.

Electron Velocities, The Influence of Contact Difference of Potential on the Measurement of, in the Photoelectric Effects, *Karl T. Compton*, 449.

Electroscope, A New Form of Gold-leaf, A Null Instrument, *J. C. Hubbard*, 558.

Entladungsstrahlen at Atmospheric Pressure and at Diminished Pressures, *Elizabeth R. Laird*, 512.

Errata, 563.

Evaporation of Water, Heat of, *Arthur Whitmore Smith*, 173.

Ewell, Arthur, W., Torsional Rotatory Polarization, 451.

Artificial Rotatory Polarization, 480.

F.

Fletcher, Harvey, A Verification of the Theory of Brownian Movements and a Direct Determination of the Value of *NE* for Gaseous Ionization, 81.

Frictional Force, The Measurement of the, Exerted on a Sphere by a Viscous Fluid, when the Center of the Sphere Performs Small Periodic Oscillations along a Straight Line, *George F. McEwen*, 492.

G.

Gage, Henry Phelps, The Radiant Efficiency of Arc Lamps, 111.

Grondahl, L. O., The Thermoelectric Behavior of Heusler Alloys in a Magnetic Field, 531.

H.

Harkins, M. R., The Transmission of Sound through Porous and Nonporous Materials, 128.

Heusler Alloys, The Thermoelectric Behavior of, in a Magnetic Field, *L. O. Grondahl* and *S. Karrer*, 531.

High Temperatures, Thermal Conductivity at, *M. F. Angell*, 421.

Hooke's Law, The Exception to, *Julien C. Smallwood*, 317.

Hubbard, J. C., A New Form of Gold-leaf Electroscope: A Null Instrument, 558.

Hulett, G. A., The Distillation of Amalgams and the Purification of Mercury, 307.

I.

Induction, Increase of Magnetic, in Nickel Bars due to Transverse Joints, *E. H. Williams*, 60.

Ions, On the Presence in Point Discharge, of Opposite Sign, *John Zeleny*, 70.

Ionization, The Positive, from Hot Salts, *O. W. Richardson*, 450.

Ives, Herbert E., Spectral Luminosity Curves Determined by the Method of Critical Frequencies, 561.

J.

Johnson, Arden Richard, On the Dissolution of a Metal in a Binary Solution, one Component Acid, 27.

K.

Karrer, S., The Thermoelectric Behavior of Heusler Alloys in a Magnetic Field, 531.

Kunz, Jakob, On the Positive Potential of Metals in the Photoelectric Effect and the Determination of the Wavelength Equivalent of Roentgen Rays, 208.

L.

Laird, Elizabeth R., Entladungsstrahlen at Atmospheric Pressure and at Diminished Pressures, 512.

Langford, Grace, The Selective Reflection of Ortho-, Meta- and Pyro-phosphate in the Infra-red Spectrum, 137.

Littleton, J. T., Jr., The Optical Constants of Alloys as a Function of Composition, 453.

Luminescence, Studies in, XVI. The Fluorescence and Absorption of Certain Uranyl Salts. *Edw. L. Nichols* and *Ernest Merritt*, 354.

Luminosity Curves, Spectral, determined by the Method of Critical Frequencies, *Herbert E. Ives*, 561.

M.

McEwen, George F., The Measurement os the Frictional Force Exerted on a Sphere by a Viscous Fluid, when the Center of the Sphere Performs Small Periodic Oscillations Along a Straight Line, 492.

McGinnis, C. S., The Transmission of Sound through Porous and Non-porous Materials, 128.

McKeehan, L. W., The Terminal Velocity of Fall of Small Spheres in Air at Reduced Pressures, 153.

Mendenhall, C. E., Notes on Optical Pyrometry, 74.

On the Fusion of Carbon, 65.

Mercury, The Distillation of Amalgams and the Purification of, *G. A. Hulett*, 307.

Merritt, Ernest, Studies in Luminescence. XVI. The Fluorescence and Absorption of Certain Uranyl Salts, 354.

Metals, On the Fatigue of, Subjected to Roentgen Radiation, in the Presence of Chemically Active Gases, *Edward G. Rieman*, 433.

N.

Nichols, Edw. L., Studies in Luminescence. XVI. The Fluorescence and Absorption of Certain Uranyl Salts, 354.

O.

Optical Pyrometry, Notes on, *C. E. Mendenhall*, 74.

P.

Palmer, Jr., Frederic, Note on Electrically Produced Water Ripples, 528.

Peltier, Determination of Electromotive Force for Several Metals by Compensation Methods, *A. E. Caswell*, 379.

Poynting's Theorem, A Simple Proof of, *J. F. H. Douglas*, 322.

Pyrometry, Optical, Notes on, *C. E. Mendenhall*, 74.

R.

Radiant Efficiency of Arc Lamps, *Henry Phelps Gage*, 111.

Refractive Index of Metals, *P. A. Ross*, 549.

Resistance, Note on a Variable Low, *J. H. Dellinger*, 215.

Resistance, A Method of Measuring the Fluctuations in a Rapidly Varying, *F. C. Brown* and *W. H. Clark*, 53.

Richardson, O. W., The Positive Ionization from Hot Salts, 450.

The Electron Theory of Contact Electromotive Force and of Thermoelectricity, 448.

Rieman, Edward G., On the Fatigue of Metals Subjected to Roentgen Radiation, in the Presence of Chemically Active Gases, 433.

Ripples, Note on Electrically Produced Water, *Frederic Palmer, Jr.*, 528.

Roentgen Radiation, On the Fatigue of Metals Subjected to, in the Presence of Chemically Active Gases, *Edward G. Rieman*, 433.

Roentgen Rays, On the Positive Potential of Metals in the Photoelectric Effect and the Determination of the Wavelength Equivalent of Roentgen Rays, *Jakob Kunz*, 208.

Ross, P. A., Refractive Index of Metals, 549.

Rotatory Polarization, Artificial, *Arthur W. Ewell*, 480.

Rotatory Polarization, Torsional, *Arthur W. Ewell*, 451.

S.

Saurel, Paul, On the Nomenclature of Crystallography, 203.

Selective Reflection of Ortho-, Meta- and Pyro-phosphate in the Infrà-Red Spectrum, *Grace Langford*, 137.

Selenium, Certain Characteristics of Light Negative, *Lilah B. Crum*, 538.

Selenium, The Nature of Light Action in, *F. C. Brown*, 1.

Selenium Cell, The Recovery of the Giltay, and the Nature of Light Action in Selenium, *F. C. Brown*, 403.

Smallwood, Julien C., The Exception to Hooke's Law, 317.

Smith, Alpheus W., The Transverse Thermomagnetic Effect in Nickel and Cobalt, 295.

Smith, Arthur Whitmore, Heat of Evaporation of Water, 173.

Somerville, A. A., Temperature Coefficients of Electrical Resistance, III., 77.

Sound, The Transmission of, through Porous and Non-porous Materials, *C. S. McGinnis* and *M. R. Harkins*, 128.

Sound Waves, New Records of, from a Vibrating Flame, *Joseph G. Brown*, 442.

Spheres, The Terminal Velocity of Fall of Small, in Air at Reduced Pressures, *L. W. McKeehan*, 153.

Stewart, G. W., The Acoustic Shadow of a Rigid Sphere, with Certain Applications in Architectural Acoustics and Audition, 467.

Stifler, W. W., The Magnetization of Cobalt as a Function of the Temperature and the Determination of its Intrinsic Magnetic Field, 268.

T.

Temperature Coefficients of Electrical Resistance, *A. A. Somerville*, 77.

Thermal Conductivity at High Temperatures, *M. F. Angell*, 421.

Thermoelectric Behavior of Heusler Alloys in a Magnetic Field, *S. Karrer*, 531.

Thermomagnetic Effect, The Transverse, in Nickel and Cobalt, *Alpheus W. Smith*, 295.

U.

Uranyl Salts, The Fluorescence and Absorption of Certain, *Edw. L. Nichols* and *Ernest Merritt*, 354.

V.

Virial Theorem, A New, *D. F. Comstock*, 557.

W.

Water, Heat of Evaporation of, *Arthur Whitmore Smith*, 173.

Watts, O. P., On the Fusion of Carbon, 65.

Williams, E. H., Increase of Magnetic Induction in Nickel Bars due to Transverse Joints, 60.

Worthing, A. G., Some Thermodynamic Properties of Air and of Carbon Dioxide, 217, 563.

Wright, J. R., The Positive Potential of Aluminum as a Function of the Wave-length of the Incident Light, 43.

Z.

Zeleny, John, On the Presence in Point Discharge of Ions of Opposite Sign, 70.

3 2044 102 920 824